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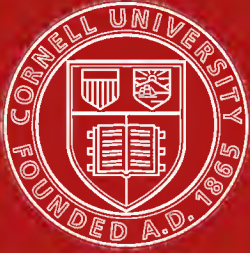
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*MANUALS OF CHEMICAL TECHNOLOGY.—II.*

EDITED BY GEOFFREY MARTIN, Ph.D., D.Sc., B.Sc.

# THE RARE EARTH INDUSTRY

Including the Manufacture of Incandescent Mantles,  
Pyrophoric Alloys, and Electrical Glow Lamps

BY

*SYDNEY J. JOHNSTONE, B.Sc. (London)*

*Senior Assistant, Scientific and Technical Department,  
Imperial Institute, London*

TOGETHER WITH A CHAPTER ON

## THE INDUSTRY OF RADIOACTIVE SUBSTANCES

BY

*ALEXANDER S. RUSSELL, M.A., D.Sc.*

*Late Carnegie Research Fellow, and 1851 Exhibition  
Scholar of the University of Glasgow*



LONDON

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1915

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## P R E F A C E

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THE present volume on the Rare Earth Industry is the second of a projected series of manuals on Industrial Chemistry, designed to give concise but sufficient information concerning the manufacture and utilisation of certain chemical products, whose exploitation has been hitherto but little developed in this country.

The book is essentially of a practical nature, and confines itself more especially to the industrial applications of the rare earths, the pure chemistry of these numerous substances being only dealt with in so far as is necessary for properly understanding the nature and properties of the materials dealt with.

A special point has been made of giving references to the more important patents, both British and foreign, which deal with manufacturing details. Moreover, numerous references to current literature are given, which will enable the reader to trace any details back to the original authorities.

The importance at the present time of the rare earths and radioactive substances can hardly be over-estimated. Out of their technical utilisation most important industries have recently arisen, the whole subject of gas and electrical lighting has been revolutionised, the match industry has been attacked, while certain branches of surgery and medicine have entirely changed

their course within a few years. With the advent of the rarer elements into technology, moreover, has dated the discovery of a whole series of very remarkable steels, which have again reacted on the engineering industries, and on the progress of invention in a way which at present it is difficult to adequately estimate.

Owing to the absence of Dr Russell on active service, the responsibility of seeing the chapter on "The Industry of Radio-active Substances" through the press has fallen upon the Editor, who has also made several additions to the article. Thus, a short note on the history of the subject (p. 112) has been added, as well as a list of the principal patents relating to the radio-active substances.

THE EDITOR.

*June* 1915.

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# INTRODUCTION

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**T**HE term "Rare Earths" is usually understood by chemists to denote the oxides of a large group of elements, which in their chemical and physical properties exhibit a very great similarity to each other; these elements usually occur associated together in minerals.

The "rare earths" are usually classified into two groups: (1) **The Cerium Earths**; (2) **The Yttrium Earths**. To the first group the following elements belong: Cerium, lanthanum, praseodymium, neodymium, and samarium. To the second group belong: Yttrium Europium, terbium, dysprosium, gadolinium, holmium, erbium, thulium, ytterbium, and scandium.

It is the usual custom to classify the oxides of thorium and zirconium with the rare earths. We also, for convenience sake, include in the group the technically important elements such as tantalum, tungsten—although, strictly speaking, these do not belong to the series.

It is almost impossible to discuss the industrial utilisation of the "rare earths" in a satisfactory manner without including some account of certain other metals. Thus, an account of thorium would be incomplete without some description of recent important developments in the utilisation of thorium-tungsten alloys as filaments for incandescent electric glow lamps, and a comparison of these with the pure tungsten and tantalum filaments. Chapters have therefore been included dealing with tungsten, tantalum, and the chemical aspects of the incandescent electric lamp industry. Similarly, the close association of uranium and vanadium with the industry of radioactive materials renders an account of these desirable.

In the following pages we only consider those rare elements which are of industrial importance. Treatises on pure chemistry will supply the readers with the chemistry of the other members of the series.

It should, however, be mentioned here that the term "rare earths" is a misnomer. The term dates from the time when chemists were only acquainted with small quantities of the minerals containing these elements—such as gadolinite, orthite, cerite, etc.—which occur only very rarely in a few localities.

However, with the rise into importance of the "rare earths," other supplies have been found in large quantities, and at the present time many

of these "rare" earth elements are obtainable in larger quantities and at a cheaper rate than many so-called "common" elements.

The rare earth industry was founded by Auer von Welsbach some twenty-five years ago, when he discovered the illuminating effect of the oxides of thorium and cerium, and applied them to the manufacture of gas mantles. The industry has steadily developed since that date, until, at the present time, it employs many thousands of workmen throughout the globe, and has developed into many curious side lines.

However, it is not the purpose of this volume to deal with the historical side of the question. The reader interested in such matters will find full details in the many larger works on the various branches of the subject which are now accessible, and to which reference is given in the following pages.

Recent events have demonstrated the desirability of manufacturers having some knowledge of sources of raw material, other than those from which the supply is usually obtained. An attempt has therefore been made to mention briefly such possible sources, and to indicate where further information can be found.

The commercial values of the raw materials and costs of production given in the text are for the normal conditions which prevailed prior to the outbreak of war.

No attempt has been made to give exhaustive accounts of the methods of chemical analysis which could be employed for the examination of the various ores and products, but examples are quoted in order to indicate the methods involved. Thanks are due to the numerous manufacturers who have kindly supplied details of recent developments in their several branches of technology.

S. J. J.

"ROUSDON,"

CLIFFORD ROAD,

NEW BARNET,

HERTS.

# LIST OF PRINCIPAL JOURNALS ABSTRACTED

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<i>Abbreviation.</i>	<i>Journal and Place of Publication.</i>
Amer. Journ. Sci.	American Journal of Science (Newhaven, Conn., U.S.A.),
Annalen	Annalen der Chemie (Leipzig).
Analyst -	Analyst (London).
Ann. Chim. Phys.	Annales de Chimie et de Physique (Paris).
Ann. des Mines	Annales des Mines (Paris).
Ber.	Berichte der Deutschen Chemischen Gesellschaft (Berlin).
Bull. Amer. Inst. Min. Eng.	Bulletin of the American Institute of Mining Engineers (Philadelphia).
Bull. Imp. Inst. -	Imperial Institute Bulletin (London).
Brit. Med. Journ.	British Medical Journal (London).
Bull. Soc. Ind. Mulhouse	Bulletin de la Societie Industrielle de Mulhouse (Paris).
Bull. Soc. d'Encour.	Bulletin de la Societe d'Encouragement pour l'Industrie Nationale (Paris).
Bull. Soc. Min. -	Bulletin de la Société française de Minéralogie (Paris).
Centralbl. Min. -	Centralblatt für Mineralogie, Geologie, und Paläontologie (Stuttgart).
Chemische Ind. -	Chemische Industrie (Berlin).
Chem. News	Chemical News (London).
Chem. World	Chemical World (London).
Chem. Zeit.	Chemiker-Zeitung (Cöthen).
Collegium	Collegium (Worms am Rhein.).
Col. Reps. Misc. Ser.	Colonial Office Reports, Miscellaneous Series (London).
Comptes rend.	Comptes-Rendus hebdomadaires des Seances de l'Academie des Sciences (Paris).
Dingler's Polytech. Journ.	Dingler's Polytechnic Journal (Stuttgart).
Dental Review	Dental Review (Chicago, U.S.A.).
Electrical Engineer	Electrical Engineer (London).
Elec. Journ.	Electric Journal (Pittsburg, U.S.A.).
Electrical Review	Electrical Review (London).
Electrician -	Electrician (London).
Econ. Geol. -	Economic Geology (Newhaven, Conn., U.S.A.).
Färber-Zeit.	Färber-Zeitung (Berlin).
Gaz. Chim. Ital.	Gazzetta Chimica Italiana (Rome).
Gerber -	Gerber (Vienna).
Helios	Helios (Leipzig).
Jahres. über Fortschr.	Jahresbesicht über die Fortschritte der Chemie.
Jb. Min.	Neues Jahrbuch für Mineralogie, Geologie, und Paläontologie (Stuttgart).
Journ. Amer. Chem. Soc.	Journal of the American Chemical Society (Washington).
Journ. Chem. Soc.	Journal of the Chemical Society (London).
Journ. Chim. Phys.	Journ de Chimie Physique (Paris).
Journ. für Gasbel.	Journal für Gasbeleuchtung und Wasserversorgung (München).

<i>Abbreviation.</i>	<i>Journal and Place of Publication.</i>
Journ. Gas Lighting	Journal of Gas Lighting (London).
Journ. Indus. and Eng. Chem.	Journal of Industrial and Engineering Chemistry (Washington, U.S.A.).
Journ. prakt. Chem.	Journal für praktische Chemie (Leipzig).
Journ. Soc. Chem. Ind.	Journal of the Society of Chemical Industry (London).
Journ. Soc. Dyers.	Journal of the Society of Dyers and Colourists (Bradford).
Leather Trades Review - Metallurgie	Leather Trades Review (London).
Metall und Erz	Die Metallurgie (Halle a/S).
Met. and Chem. Eng.	Metall und Erz (Halle a/S, Germany).
	Metallurgical and Chemical Engineering (New York, U.S.A.).
Min. Ind.	Mineral Industry (New York, U.S.A.).
Min. Journ.	Mining Journal (London).
Min. Mag.	Mineralogical Magazine (London).
Min. Res. U.S. -	Mineral Resources of the United States (Washington, D.C.).
Monatsh.	Monatshefte für Chemie der kaiserlichen Akademie der Wissenschaften, Wien (Vienna).
Oester. Zeit. für Berg und Huttenwesen	Oesterreichische Zeitschrift für Berg und Hüttenwesen (Vienna).
Phil. Mag.	Philosophical Magazine (London).
Proc. Amer. Inst. Chem. Eng. -	Proceedings of the American Institute of Chemical Engineers.
Proc. Amer. Inst. Elec. Eng.	Proceedings of the American Institute of Electrical Engineers.
Proc. Inst. Min. and Met.	Proceedings of the Institution of Mining and Metal- lurgy (London).
Proc. Roy. Instit. Gt. Brit.	Proceedings of the Royal Institution of Great Britain (London).
Proc. Roy. Soc.	Proceedings of the Royal Society (London).
Rec. Geol. Sur. India	Records of the Geological Survey of India (Calcutta).
Science	Science.
Stahl und Eisen -	Stahl und Eisen (Düsseldorf).
Textile Colourist	Textile Colourist.
Trans. Amer. Ceram. Soc.	Transactions of the American Ceramic Society (Columbus, U.S.A.).
Trans. Amer. Electrochem. Soc.	Transactions of the American Electrochemical Society (South Bethlehem, Pa., U.S.A.).
Trans. Amer. Foundrymen's Assoc.	Transactions of the American Foundrymen's Association (Watchung, N.J. U.S.A.).
Trans. Inst. Metals	Transactions of the Institute of Metals (London).
Trans. Iron and Steel Inst.	Transactions of the Iron and Steel Institute (London).
U.S. Bur. Mines Bulls. -	United States Bureau of Mines Bulletins (Washington, D.C.).
Zeits. anal. Chem.	Zeitschrift der analytischen Chemie (Wiesbaden).
Zeits. angew. Chem.	Zeitschrift für angewandte Chemie (Leipzig).
Zeits. anorg. Chem.	Zeitschrift der anorganischen Chemie (Leipzig).
Zeits. Chem. Ind. Kolloide	Zeitschrift für Chemie und Industrie de Kolloide (Dresden).
Zeits. Elektrochem.	Zeitschrift für Elektrochemie und angewandte physikal- ische Chemie (Halle, a/S).
Zeits. prakt. Geol.	Zeitschrift für praktischen Geologie (Berlin).
Zeits. physik. Chem.	Zeitschrift für physikalische Chemie (Leipzig).



## CHAPTER I



# The Thorium and Cerium Industry



# CHAPTER I

## THE THORIUM AND CERIUM INDUSTRY

### Including the Manufacture of Incandescent Mantles and Pyrophoric Alloys

#### LITERATURE

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#### THORIUM

This element, in the form of its nitrate,  $\text{Th}(\text{NO}_3)_4 + 4\text{H}_2\text{O}$ , is by far the best known and most widely used of the rare earths. This is due, of course, to its employment in the manufacture of mantles for incandescent gas lighting.

The oxide, thorium ( $\text{ThO}_2$ ), was discovered by Berzelius in 1828, in the mineral now known as **thorite**, but it was not until 1885, when Auer von Welsbach invented the incandescent mantle, that a commercial use was found for the material.

#### Natural Occurrence

At the time when Welsbach invented the incandescent mantle, the only sources of thorium were certain rare earth minerals, such as monazite, thorite, æschynite, samarskite, gadolinite, etc., found chiefly in Scandinavia. As these occurred only in small quantities, it was obvious that this source of supply would not be able

to keep pace with the demand. A search for suitable material led to the important discovery of large deposits of **monazite** on certain parts of the sea-coast of Brazil, which for many years formed the source of practically all the thorium of commerce. Small quantities of **thorianite** and **thorite** are also used for this purpose.

**Monazite** is a mineral composed essentially of phosphates of the cerium and lanthanum earths, together with a small and variable percentage of thorium. Its colour varies from golden yellow to dark reddish brown, and occasionally black. Its specific gravity varies from 4.8 to 5.5; samples having the higher specific gravity usually contain a large percentage of thorium (see Table I.).

Although monazite is known to occur *in situ* in certain gneissic and granitic rocks, the deposits now worked are all of an alluvial character. The most important deposits are those situated on the sea-coast of Brazil, particularly those in **Bahia, Espírito Santo, and Rio de Janeiro**, where the sands, which occur as the result of the weathering of the monazite-containing rocks, are naturally concentrated by tidal action. This concentration takes place by virtue of the difference in specific gravity between the monazite and the associated minerals, which include quartz, zircon, garnet, rutile, tourmaline, etc. The percentage of monazite in these sands naturally varies between wide limits, and may be as low as 2 per cent. or as high as 60 per cent. The mineral occurs mostly in the form of fine grains, each under 1 mm. in diameter.

Extensive deposits of the mineral also occur inland, but so far these appear to have been but little worked, possibly owing to transport difficulties and the higher grade and greater ease of working of the coastal deposits. These deposits, which are largely covered with dense forest, occur in beds of gravel, 4-6 ft. thick, which contain from 2-4 per cent. of monazite. For accounts of the Brazilian deposits and their working, articles by F. Freise, *Oester. Zeit. für Berg & Hüttenwesen*, 1911, p. 27, and *Zeits. prakt. Geol.*, 1909, 17, 514, should be consulted.

The Brazilian coastal deposits are now worked under a fifteen years' contract, from 1912, from the Brazilian Government, the contractors engaging to export at least 35,000 tons during that period. The Government is to receive a royalty of £120,000 on the first 27,000 tons exported, and 50 per cent. of the net profits on the thorium nitrate manufactured from the sand.

In the past, attempts to obtain the control of these deposits have led to an enormous amount of plotting, and, for many years, the whole output passed into German hands, and so practically the whole of the world's consumption of thorium nitrate was made in Germany. Recently a large proportion has been made in France, and an American company has also obtained a small proportion of the Brazilian output.

In North America, important deposits of monazite have been located and worked in **North and South Carolina**, but owing to the fact that a decrease in the price of thorium nitrate rendered the working unremunerative in many localities, the deposits have not been worked recently to any appreciable extent. The monazite, which occurs in crystals about the size of a pea, is found in gravels lying about 4 ft. from the surface and varying in thickness from 1 to 10 ft. A full account of these deposits is given by J. H. Pratt in *Economic Paper No. 14, North Carolina Geological Survey*.

In **Travancore**, Southern India, important deposits of monazite, containing nearly twice as much thorium as the Brazilian mineral, have been located and worked near Cape Comorin and Ashtamudi Bar. These deposits now occupy an increasingly important place among the countries producing monazite (see Table V.), and have been described in *Report of State Geologists of Travancore* for 1907-10 (Trivandrum, 1910), and by G. H. Tipper in *Records of Geological Survey, India*, 1914, 44, 186.

The mineral has also been found in several other countries, e.g., Norway, Ceylon, Nigeria, Nyasaland, South Africa, Australasia, Russia, and Malaya, but none of these countries figure as important producers at the present time.

The following are the results obtained by the author in the examination of

**Monazites from new localities** in Ceylon, Travancore, Malaya, Nigeria, and Nyasaland (*Journ. Soc. Chem. Ind.*, 1914, **33**, 56).

These analyses were all made, at the Imperial Institute, on the pure monazite separated from the associated minerals. Results are also given of the examination of samples of pure monazite from two of the more important producing localities in Brazil. In these analyses any uranium present in the mineral is included in the figure for alumina.

TABLE I.—CEYLON MONAZITE

Locality		1. Monazite Pebble from Naminkanda Morawak Korle.	2. Monazite Pebble from Muladiwa- nella Duraya- kanda, Gilimale.	3- Sand from Niriella Ganga.	4- Monazite Pebble from Ratnapura.	5- Monazite Pebble from Ratnapura.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Thoria	ThO <sub>2</sub>	9.75	9.49	10.75	10.29	28.20
Ceria	Ce <sub>2</sub> O <sub>3</sub>	27.51	27.15	26.71	27.37	20.65
Lanthana and allied oxides	La <sub>2</sub> O <sub>3</sub> , etc.	29.59	29.59	30.06	30.13	21.63
Yttria and allied oxides	Y <sub>2</sub> O <sub>3</sub> , etc.	2.54	3.93	1.46	2.14	0.94
Ferric oxide	Fe <sub>2</sub> O <sub>3</sub>	1.27	0.87	1.09	0.81	1.13
Alumina	Al <sub>2</sub> O <sub>3</sub>	0.61	0.17	0.70	0.17	0.29
Lime	CaO	...	0.45	0.85	0.41	0.10
Silica	SiO <sub>2</sub>	1.78	1.67	2.47	1.03	6.09
Phosphoric acid	P <sub>2</sub> O <sub>5</sub>	26.12	26.12	24.61	27.67	20.20
Loss on ignition	...	6.59	0.48	0.93	0.20	...
Specific gravity	...	5.20	5.25	...	5.23	5.47

From these results it is evident that the Ceylon monazite usually contains about 10 per cent. of thoria, which is nearly double the amount found in the monazite of Brazil. It must be mentioned, however, that as little as 5 per cent. of thoria has been found, by the author, in fine grained monazite isolated from certain sands from Ceylon, but material of this character appears to be of somewhat infrequent occurrence. Occasionally, specimens are met with having an unusually high specific gravity and a correspondingly high percentage of thoria, which it will be seen has reached over 28 per cent. (column 5 in Table I.).

TABLE II.—NIGERIAN MONAZITE

Number	Northern Nigeria.			Southern Nigeria.		
	1.	2.	3.	4.	5.	6.
Locality	Ekole.	Kadera, Central Province.	Jarawa River, Naraguta.	Iboboto Stream, Nsan-Oban Track.	Between Iboboto Stream and Ebara River.	Ebara River.
Thoria -	Per Cent. 5.00	Per Cent. 3.20	Per Cent. 8.00	Per Cent. 6.19	Per Cent. 2.30	Per Cent. 5.50
Ceria	30.72	36.53	30.50	30.38	34.58	31.40
Lanthana and allied oxides	30.02	30.00	28.80	29.60	29.83	29.20
Yttria and allied oxides	2.74	0.39	1.43	1.33	1.29	2.00
Ferric oxide -	3.00	1.20	0.81	1.50	1.80	0.75
Alumina	0.35	0.10	0.20	0.10	...	0.05
Lime	0.15	0.21	0.17	0.16	0.19	0.10
Silica	1.20	0.63	1.79	0.85	0.73	0.82
Phosphoric acid	26.29	28.29	28.16	29.70	29.71	29.92
Loss on ignition	0.25	0.20	0.21	0.33	0.21	0.44

The above results show that the percentage of thorium in monazite from Nigeria may vary between fairly wide limits. The average thorium content of a large number of Nigerian monazites examined by the author was 5.5 per cent. for those from Northern Nigeria and 5.8 per cent. for those from Southern Nigeria. The results show that these monazites, as a whole, are nearly as rich in thorium as those exported from Brazil.

TABLE III.

Locality	Malayan Monazite.				Travancore Monazite.		Nyasaland Monazite.	Brazilian Monazite.	
	Pahang.	Puchong Babi, River Kenring, Perak.	Kulim, Kedah.	Kelantan.				Espirito Santo.	Alcobaca, Bahia.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Thorium	8.38	3.40	3.53	9.41	10.22	8.65	7.10	6.06	6.50
Ceria	25.46	33.74	64.05	60.00	31.90	61.11	32.52	62.12	61.40
Lanthana and allied oxides	32.72	32.53			28.00		26.91		
Yttria and allied oxides	2.80	0.91	2.40	2.82	0.46	0.62	1.50	0.80	0.70
Ferric oxide	0.84	0.65	0.64	1.13	1.50	1.09	1.10	0.97	1.50
Alumina	2.78	0.03	0.07		0.17	0.12	0.20	0.10	0.08
Lime	0.61	0.33	0.17	0.29	0.20	0.13	0.32	0.21	0.30
Silica	0.92	1.45	1.08	2.20	0.90	1.00	1.66	0.75	0.64
Phosphoric acid	23.92	26.58	27.87	23.71	26.82	26.50	28.16	28.50	28.46
Loss on ignition	1.28	0.94	0.52	0.94	0.46	0.45	0.25	0.38	0.64

From the results of numerous partial analyses made by the author on other samples of monazite from Nyasaland, it would appear that the average thorium content is about 6 per cent.

The analyses of Travancore monazite show that it contains a high percentage of thorium approaching that of ordinary Ceylon monazite. According to E. White (*Thorium and its Compounds*, p. 10) from 6 to 14 per cent. of thorium has been found in Travancore monazite.

Monazite from South Africa is usually poor in thorium; in some samples the amount of this constituent present is under 1 per cent. Samples of the mineral from Australia often contain only 2 or 3 per cent. of thorium.

**Preparation of the Sand for Export.**—As stated above, the crude sand may contain from 2 to 60 per cent. of monazite, but in order to be saleable under present conditions, it is necessary for the raw material to contain at least 4 per cent. of thorium. As the pure Brazilian monazite usually contains between 5 and 6 per cent. of thorium, it is evident that the sand must be concentrated so as to contain at least 70 per cent. of the pure mineral, and in practice it is more usual to dress the sand so that it contains about 90 per cent. of monazite. In the deposits, the monazite is usually associated with a large percentage of quartz, together with some ilmenite, garnet, rutile, zircon, hornblende, etc., and the method of concentration employed varies largely according to which of these minerals is present and the average size of the monazite grains. In general, three processes are in use, at the present day, for effecting this concentration. (1) **Wet processes** involving the use of shaking tables of the Wilfley type. (2) **Dry blowing**. (3) **Electromagnetic means**.

In the **wet process** the sand is run, with a stream of water, on to one corner of the rectangular concentrating table (see Fig. 1), which is tilted so that the material travels diagonally across it. The individual minerals, assisted by a jiggling motion which is mechanically imparted to the table, during their passage across the table arrange themselves roughly in order of their specific gravities.

The defect of this and similar wet concentration processes is that small particles of high specific gravity tend to behave in the same way as larger particles of lower specific gravity, and so an efficient separation, in the case of monazite, is difficult to carry out without losing a fair amount of the mineral as tailings.

In Brazil, the **initial concentration** is often performed by a **wet process** and the concentrates are then raised to a marketable grade by means of **electromagnetic separation**.

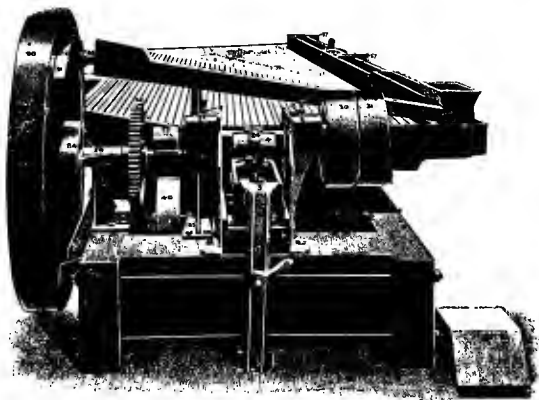


FIG. 1.—Movement End of Wilfley Table.

In **dry blowing**, the principle of concentration by gravity is here also employed as in wet concentration, but a blast of air is used in place of a current of water. This process has been used, with considerable success, in Travancore for concentrating monazite.

A machine, which is in use in Travancore, is illustrated in Fig. 2. Air from a suction blower enters the table from below and passes through the pervious cloth top, forming a film of air, under

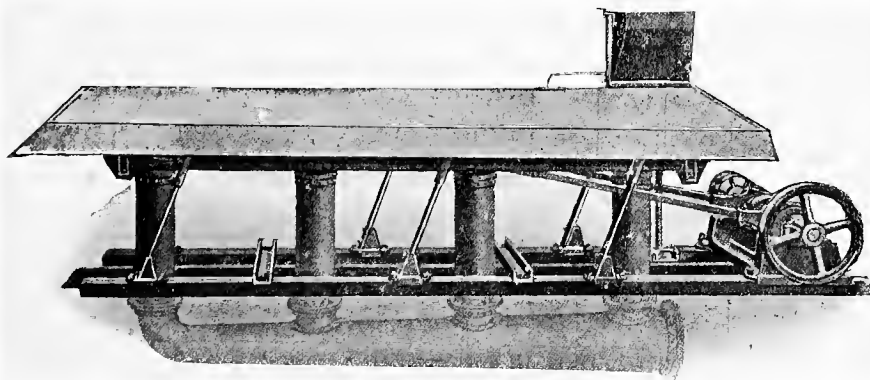


FIG. 2.—Sutton-Steele Dry Concentrating Table.

pressure, on the upper surface of the cloth. This air film causes the minerals to arrange themselves vertically, in order of their specific gravities; the heaviest being at the bottom. A reciprocating motion is also imparted to the table, thus causing the minerals to separate into zones.

A full description of the process of dry blowing is given by R. H. Richards, "Ore Dressing," vol. ii., p. 815 (New York, 1903).

**Electro-magnetic separation** is usually the most satisfactory method of producing a high-grade monazite concentrate, although the initial outlay for plant

is much greater than is required for either of the foregoing processes. This method is based upon the fact that many minerals differ in magnetic permeability, *i.e.*, a current which will attract certain minerals will leave others unaffected.

A machine suitable for the purpose is shown in Fig. 3, and its action can be seen by reference to the diagrammatic sketch, Fig. 4. The well-dried sand is fed from the hopper in an evenly distributed layer on to the band B.1, and is carried forward and thrown against the belt B.2, which travels just beneath the poles of the electro-magnet S.S. The constituent minerals of the sand are

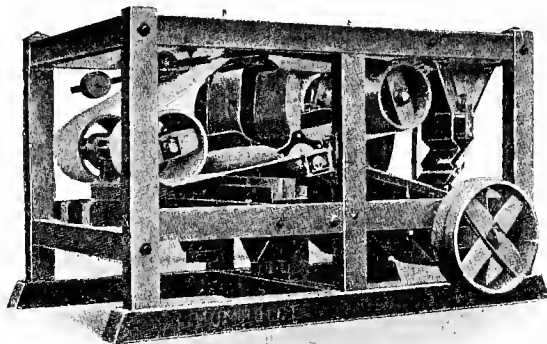


FIG. 3.—Wetherill Magnetic Separator.

attracted towards the magnet in varying degrees and fall into the collecting boxes arranged below, in order of their permeability. By repeating this treatment twice a product containing from 90 to 95 per cent. of pure monazite can be usually obtained.

**Thorianite** is a heavy black mineral usually found in small cubes, having a specific gravity of about 9.5 and a hardness of 7. It is usually readily soluble in either nitric or sulphuric acid. The mineral was first found in certain stream beds and gem-bearing gravels in the Central, Sabaragamuwa, and Southern provinces of **Ceylon**. It has also been found, recently, in a placer deposit on the river Boshagoch

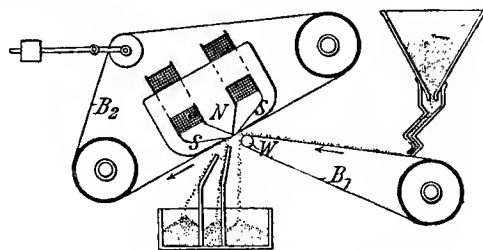


FIG. 4.—Wetherill Separator (Diagrammatic).

in Transbaikal, **Russia**. In 1905, about 9 tons of the mineral was exported from Ceylon and sold at prices varying from £1,600 to £1,700 per ton; but since then only small quantities have been produced. Thorianite is of interest, as containing a higher percentage of thorium than any other known mineral (see Table IV.).

For a full account of this mineral, see W. R. Dunstan and G. S. Blake, *Proc. Roy. Soc.*, 1905, A, 76, 253, and W. R. Dunstan and B. M. Jones, *Proc. Roy. Soc.*, 1906, A, 77, 546.

**Thorite** consists essentially of thorium silicate,  $\text{ThO}_2, \text{SiO}_2$ ; in colour it varies from yellow to dark brown, and its specific gravity may be between 4.4 and 5.4



It is of little importance as a source of thorium owing to the small quantity available, but it is occasionally exported from **Southern Norway and Ceylon**. Its composition is shown in Table IV.

TABLE IV.

	Formula.	Ceylon Thorianite.		Ceylon Thorite.	
		1.	2.	3.	4.
Thorium -	ThO <sub>2</sub>	Per Cent. 58.84	Per Cent. 78.86	Per Cent. 71.04	Per Cent. 70.12
Ceria and allied oxides	Ce <sub>2</sub> O <sub>3</sub> , etc.	0.85	1.02	1.89	2.32
Ferric oxide	Fe <sub>2</sub> O <sub>3</sub>	1.31	0.46	3.67	1.93
Uranium oxide	U <sub>3</sub> O <sub>8</sub>	32.74	15.10	0.77	5.38
Lime -	CaO	0.19	1.13	...	...
Lead oxide -	PbO	2.56	2.59	...	1.40
Silica -	SiO <sub>2</sub>	0.45*	0.20	13.35	13.30
Phosphoric acid	P <sub>2</sub> O <sub>5</sub>	...	...	2.02	1.60
Loss on ignition	...	1.26	...	7.16	4.59
Specific gravity	...	...	...	4.94	5.94

1 Dunstan and Jones, *loc. cit.*

2 Dunstan and Blake, *loc. cit.*

3 and 4 "Rep. Min. Sur. Ceylon," Col. Repts. Misc. Ser. (Cd. 3190, also Cd. 7175).

**Commercial Value of Thorium Minerals.**—In 1912, 75 per cent. of the world's annual production of monazite sand came from Brazil (Espírito Santo and Bahia). This being the case, the price obtainable for the raw material from other sources has, in the past, been largely controlled by the shipments from Brazil. As is often the case with the less common minerals, the price obtainable is largely a matter of negotiation between the parties, but as a rough guide it may be stated that at the present time (June 1914), concentrates carrying 90 per cent. of monazite and not less than 4 per cent. of thorium can be sold at about £4 per unit, per cent., of thorium (ThO<sub>2</sub>), *i.e.*, a concentrate carrying 4.5 per cent. of thorium would fetch £18 per ton, c.i.f. United Kingdom ports. In the case of such minerals as thorianite, which contain a much larger percentage of thorium (see analyses, Table IV.), a higher price per unit can often be obtained, providing, of course, that the material is not unusually refractory, and does not contain minerals, such as mica, which cause difficulty in the process of manufacturing thorium nitrate (see p. 11).

**Production.**—The output, during recent years, of monazite sand from the more important producing countries is shown in the following table:—

TABLE V.

	1909.		1910.		1911.		1912.	
	Metric Tons.	Value.	Metric Tons.	Value.	Metric Tons.	Value.	Metric Tons.	Value.
Brazil -		£		£		£		£
United States	6,462	144,742	5,437	127,526	3,686	111,104	3,398	108,758
Travancore (S. India)	246	13,548	45.1	2,501	1.6	89	0.5	33
	...	...	...	...	832	24,044	1,135	41,419

\* Insoluble matter.

The value and original destination of the monazite shipped from Brazil, during recent years, is shown in the following table :—

TABLE VI.

Destination.	1910.		1911.		1912.	
	Metric Tons.	Value Reis.	Metric Tons.	Value Reis.	Metric Tons.	Value Reis.
Germany	2,636	921,069	1,890	868,343	1,852	900,070
France	1,691	592,321	1,096	485,016	944	440,680
United States	1,100	387,200	700	316,400	600	257,400
Great Britain	...	...	...	...	1.2	600
Italy	10	3,582	...	...	...	...

1 reis = 1s. 4d.

The total quantity of monazite exported from Brazil during 1913 amounted to 1,437 metric tons, valued at £38,444.

The whole of the Travancore output has, for several years past, gone entirely to Germany.

**Analysis of Thorium Minerals.**—The complete analysis of a thorium mineral is usually a long and tedious operation requiring much experience if accurate results are to be obtained, and the necessary operations are too complicated to be described here in detail.

A method for the complete analysis of monazite sand, which permits of the whole operation being carried out on one portion of the sample, has been described recently by the author (*Journ. Soc. Chem. Ind.*, 1914, 33, 56), and is briefly as follows :—

The finely ground mineral is digested with hot concentrated sulphuric acid until all the monazite has been decomposed, and the pasty mass of sulphates is then treated with cold water. After separation of the insoluble silica, by filtration, the rare earths in the acid solution are precipitated by means of ammonium oxalate. Thorium is estimated in this precipitate by the thio-sulphate method (see standard method given below). The cerium, lanthanum, and yttrium earths in the thio-sulphate filtrate are recovered by treating the solution with concentrated nitric acid, and then precipitating them by means of ammonia. Yttrium is separated from the cerium and lanthanum in this precipitate by fractional crystallisation of the double potassium sulphates, the yttrium salt remaining in solution. Cerium is separated from the lanthanum and didymium earths by converting all to hydroxides and treating with a current of chlorine whilst suspended in a fairly strong solution of caustic potash. This treatment causes the lanthanum and didymium earths to pass into solution whilst the cerium is converted into the insoluble hydrated peroxide. The filtrates from the precipitation with ammonium oxalate contain the iron, aluminium, calcium, and phosphoric acid, and after destroying the oxalate, by evaporation to dryness with nitric acid, these constituents are estimated by the ordinary methods of analysis. The accurate quantitative estimation of thorium in monazite is now a matter of considerable technical importance, and the following detailed account by E. White ("Thorium and Its Compounds"), of a variation of the thio-sulphate method, may be quoted, as it is stated to be the standard process employed commercially.

**Standard Method.**—12.5 gm. of sand are heated to 180° to 200° C. for two or three hours, or until all monazite grains are "broken," with 50 c.c.  $\text{H}_2\text{SO}_4$ . (Examine a small portion mixed with water on a watch glass.) The white pasty mass is cooled and dissolved in water sufficient to produce 500 c.c. of solution when cold. Filter when cold and take 200 c.c. of the solution (equal to 5 gm. of sample), dilute with water to 500 c.c., and add, without stirring, 180 c.c. of a cold saturated solution of oxalic acid, and allow to stand until the bulky flocculent precipitate becomes heavy and crystalline (half to one hour as a rule); stir and set aside for twelve hours or overnight. Filter, reject filtrate, wash the precipitate until the washings give no reaction for phosphate with ammonium molybdate solution. (If necessary, use water acidulated with hydrochloric acid for washing). Dry and ignite the oxalates and filter paper. Dissolve the oxides in hydrochloric acid (sp. gr. 1.16) rinsing the crucible with alcohol, if necessary. Evaporate the hydrochloric solution to dryness on a water-bath, take up with a few c.c. of water, and again evaporate to dryness. Dissolve the acid-free chlorides in 200 c.c. water, and add 9 gm. of  $\text{Na}_2\text{S}_2\text{O}_3 + 5 \text{ Aq.}$  in 30 c.c. water; set aside overnight, boil for ten minutes, filter and wash the precipitate until the washings

give no reaction with ammonia. Keep both precipitate and filtrate. The filtrate is again boiled for sixty minutes, and any further precipitate formed is collected, washed, kept aside, and marked "A," the filtrate being then rejected. The precipitate produced by the ten minutes' boiling is dissolved on the filter with 5 per cent. hydrochloric acid by passing the acid several times through the filter, which is then washed with boiling water. The acid solution is evaporated to dryness on a water-bath, taken up with 150 c.c. of water, and precipitated with 3 gm. of sodium thiosulphate in 10 c.c. of water, set aside overnight, boiled ten minutes and filtered, and the filter washed with water. The filtrate is boiled after adding ammonia in excess, and the precipitated hydroxides are collected and set aside with precipitate "A" to rework. The thiosulphate precipitate is dissolved in 5 per cent. hydrochloric acid as before, evaporated, taken up, and reprecipitated with sodium thiosulphate solution, set aside, boiled, filtered, and the filtrate tested with ammonia. If the filtrate gives any precipitate with ammonia, the thiosulphate treatment is repeated until the solution gives no precipitate with ammonia. Three thiosulphate precipitations in all are generally sufficient. The final thiosulphate precipitate is dissolved on the filter in 5 per cent. hydrochloric acid, the filter washed with boiling water, and the filtrate made up to 150 c.c.; 10 c.c. hydrochloric acid are added, and then 30 c.c. of cold saturated solution of oxalic acid. The whole is kept at 30° to 40° C. for two or three hours, and then set aside overnight, filtered, and the precipitate washed, dried, and ignited. The filter papers from the thiosulphate precipitates, the precipitate "A," and all subsequent ammonia precipitates are reworked for traces of thorium which they may contain. They generally yield about 5 mg. of  $\text{ThO}_2$ , equal to 0.1 per cent. on the 5 gm. taken.

For an account of the numerous other methods which have been suggested for the separation and estimation of thorium and cerium, see "Die Analyse der seltenen Erden," by R. J. Meyer and O. Hauser (Stuttgart, 1912).

### Industrial Utilisation of Thorium Compounds

At the present time, the only commercial uses of thorium are for the production of thorium nitrate, used in the manufacture of incandescent gas mantles, the preparation of the radio-active product, mesothorium (see p. 121), alloyed with tungsten as a filament for incandescent electric lamps (see p. 84), and in certain flashlight powders.

**Manufacture of Thorium Nitrate.**—As is the case with many chemical processes, which involve the separation of a small quantity of valuable material from a large amount of comparatively worthless substance having similar chemical properties, the exact details of manufacture are carefully guarded trade secrets. The general principles involved, however, are mostly well known.

Owing to the fact that thorium occurs, in monazite, associated with members of the cerium and yttrium groups which have somewhat similar chemical properties, its separation from these is a matter of some considerable difficulty, for although there are several satisfactory methods available, on the analytical scale, these are too expensive for use on the works.

At the present time, all the processes employed for the preparation of thorium nitrate from monazite involve fractional precipitation and crystallisation at one or more stages of the operations.

The concentrated monazite, which usually contains at least 90 per cent. of the pure mineral, is first submitted to the process known as "breaking." This consists in heating it, in cast-iron pans, with about twice its weight of strong sulphuric acid (sp. gr. 1.84), until the white pasty mass of sulphates, which results from this treatment, is completely soluble in water, and no grains of yellow monazite remain. The operation is considerably facilitated if the mineral is added gradually to the *hot* acid.

**Brazilian monazite**, which occurs mostly in the form of fine grains under 1 mm. in diameter, does not usually need grinding before "breaking," but material from other sources, which is often in much larger grains, sometimes needs preliminary grinding. This is particularly the case with Carolina monazite, which often occurs in crystals about the size of a pea.

The pasty mixture of sulphates is next slowly run into cold water contained in a lead-lined vat, and the whole is well stirred until solution is complete. After allowing to stand for some time, in order to permit of the settling of the insoluble matter, which consists of silica, zircon, rutile, and other unattacked minerals, the solution of rare earth phosphates in dilute sulphuric acid is siphoned off. In this liquid the ratio of thorium to the other rare earths is about 1 to 12, and the next process consists in obtaining a product in which the ratio is about 4 to 1. This

is accomplished by taking advantage of the fact that thorium is more basic than the remaining rare earths, and so when a solution containing all these is gradually neutralised, the thorium phosphate is precipitated first. This precipitation is carried out by reducing the concentration of the free acid in the solution, either by partial neutralisation with an alkali or alkaline earth (ammonia or magnesite may be used) or by largely diluting the solution with water. The thorium precipitated in this manner is filtered off, dissolved in the minimum quantity of acid, and the fractionation repeated.

Great care is necessary in the carrying out of these operations in order to avoid losing any thorium phosphate in the waste filtrates.

The next process, involving the separation of the thorium from the phosphoric acid and remaining cerium earths, is of considerable importance, as phosphates and certain of the rare earths, particularly didymium, have a very deleterious effect on the lighting power of the incandescent mantle (see p. 15).

The methods employed, at the present time, for the removal of the phosphoric acid from this precipitate are mostly trade secrets.

A process much employed in the past was to boil the acid solution of the phosphates with oxalic acid. This caused the thorium to be precipitated as oxalate whilst the phosphoric acid remained in solution. The use of this process has now been largely discontinued, as it necessitated the use of dilute solutions and a large excess of oxalic acid, and thus proved too expensive for use on a technical scale.

An interesting process for the removal of the phosphoric acid by volatilisation, has been patented recently by C. Baskerville and described in a paper read before the Eighth International Congress of Applied Chemistry (1912, 2, 17). The process, which is being tried by the Welsbach Light Company of Gloucester City, N.J., consists in mixing one part of monazite with 1.1 parts of petroleum coke, 0.8 parts of lime, and 0.15 parts of fluorspar; heating the whole in an electric furnace for 1½ hours, using a current of 35 volts and 125 amperes. When the evolution of phosphorus ceases, the mass is allowed to cool and treated with water. Owing to the presence of calcium carbide, formed by the interaction of the lime and coke, the mass readily disintegrates to a fine powder, with the evolution of acetylene. This powder is well washed to remove calcium hydroxide, and after solution in hydrochloric acid is ready for treatment for the separation of the thorium from the cerium earths.

Previously, Muthmann, Hofer, and Weiss had operated on somewhat similar lines by fusing monazite with carbon in order to get phosphides and carbides, and then decomposing the mass with hydrochloric acid (German Patent, 129,416, 1901). Although this process removed the phosphorus, the final product was very hard and difficult to grind, probably owing to the presence of a small quantity of silicon carbide. All these difficulties are said to be overcome by Baskerville's process.

Another process which has been employed consists in fusing the phosphates with alkali carbonates and then treating the melt with water, which dissolves the sodium phosphate, leaving the rare earth oxides insoluble.

After the removal of the phosphoric acid there remains, associated with the thorium salt, from 10 to 25 per cent. of compounds of the cerium earths. There are several methods available for the separation of the thorium from this mixture. The best known of these are—(1) *Fractional crystallisation of the sulphates*. (2) *Separation by means of the double alkali carbonates*. (3) *Separation by the difference in solubility of the oxalates*.

**The Sulphate Method** of separation is based upon the property which thorium possesses of forming a number of hydrated sulphates, certain of which differ sufficiently in solubility from the sulphates of the cerium earths to make a separation possible.

Anhydrous thorium sulphate is soluble to the extent of about 25 per cent. in ice cold water, giving a labile solution. By raising the temperature of this solution various hydrates can be obtained which are much less soluble than the anhydrous sulphate or the corresponding cerium earth sulphates. At temperatures between 0° and 45° C. the thorium compound which separates out has the composition  $\text{Th}(\text{SO}_4)_2 \cdot 8\text{H}_2\text{O}$ , and between 45° and 100° C. the sulphate obtained has the composition  $\text{Th}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ . The anhydrous sulphate is prepared by heating the hydroxide with concentrated sulphuric acid to a temperature of 400° C. The product obtained is then dissolved in five parts of ice cold water, and the solution heated to 15° or 20° C.

The solubilities of these sulphates, together with those of the cerium earths, are shown in the

following table. The figures represent the quantities of the various sulphates (calculated as anhydrous) which are dissolved by 100 gm. of water at the temperatures stated :—

TABLE VII.\*

	14° to 18° C.	25° to 30° C.	42° to 50° C.
Tb(SO <sub>4</sub> ) <sub>2</sub> + 8H <sub>2</sub> O	1.38 (15°)	1.85 (25°)	3.71 (44°)
Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O	11.06 (15°)	8.39 (25°)	5.65 (42°)
Nd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O	7.10 (16°)	5.10 (30°)	3.60 (50°)
Pr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O	14.05 (18°)	10.40 (35°)	7.02 (55°)
La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 9H <sub>2</sub> O	2.60 (14°)	1.90 (30°)	1.60 (50°)

	50° to 57° C.	70° to 80° C.	90° to 100° C.
Th(SO <sub>4</sub> ) <sub>2</sub> + 4H <sub>2</sub> O	1.94 (55°)	1.09 (70°)	0.61 (90°)
Ce <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 4H <sub>2</sub> O	2.34 (57°)	1.38 (70°)	0.43 (100°)
Nd <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O	3.60 (50°)	2.70 (80°)	2.25 (100°)
Pr <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 8H <sub>2</sub> O	7.02 (55°)	4.20 (75°)	1.00 (95°)
La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> + 9H <sub>2</sub> O	1.60 (50°)	1.00 (75°)	0.70 (100°)

A consideration of these figures shows that a temperature between 15° and 20° C. is the most suitable at which to effect the separation. The octa-hydrated thorium sulphate, at this temperature, also has the advantage that it is precipitated in the form of dense crystals, which are easily washed, whilst the tetra-hydrate is usually precipitated as a woolly mass, which is more difficult to manipulate.

**The Carbonate Method** depends upon the fact that thorium carbonate forms soluble double salts with certain of the alkali carbonates, and the amount of the cerium earths which pass into solution under these conditions is very small.

Experiments carried out by O. Hehner showed that 3.375 gm. of sodium carbonate would keep in solution 0.890 gm. of thoria and about 0.002 gm. of ceria. The thorium can be recovered as oxalate from the solution of alkali carbonate by the addition of oxalic acid, or as hydroxide by means of caustic soda.

**The Oxalate Method** of separation utilises the property possessed by thorium oxalate of forming a soluble double salt with ammonium oxalate, whilst the cerium earth oxalates are almost insoluble in solutions of this salt.

The following table shows the relative quantities of the various oxalates (calculated as oxides) which are dissolved by excess of ammonium oxalate :—

ThO <sub>2</sub>	2663.0	Nd <sub>2</sub> O <sub>3</sub>	1.5
Yb <sub>2</sub> O <sub>3</sub>	105.0	Pr <sub>2</sub> O <sub>3</sub>	1.2
Y <sub>2</sub> O <sub>3</sub>	11.0	La <sub>2</sub> O <sub>3</sub>	1.0
Ce <sub>2</sub> O <sub>3</sub>	1.8		

A good account of the oxalates of the rare earths is given by B. Brauner, *Journ. Chem. Soc.*, 1898, 73, 951, and also by E. Rimbach and A. Schubert, *Zeits. physik. Chem.*, 1909, 67, 183.

From time to time various methods have been employed, in addition to the above, for the fractionation of the thorium precipitate; amongst these may be mentioned the *fractionation of the chromates* invented by W. Muthmann and E. Baur (German Patent, 120,013, 1901; English Patent, 17,603, 1902). For a description of this process, see *Ber.*, 1900, 33, 1756 and 2028.

All the above methods of separation are not quite so efficient as they would appear from the tables, owing to the fact that the relative solubilities of the thorium and cerium earth salts are not exactly maintained when these occur in solution together.

\* Compiled from figures given by Demarcay (*Comptes rend.*, 1883, 96, 1860), Roozboom (*Zeits. physik. Chem.*, 1880, 5, 198), and Wyrowboff (*Bull. Soc. Min.*, 1901, 24, 105).

After treating the thorium several times by one of the above processes, it is converted to the hydroxide or carbonate and then dissolved in nitric acid, giving the nitrate. This solution is evaporated until a drop on cooling shows signs of solidification. The solution, which is now in a state of superfusion, is allowed to cool to a certain point, and is then vigorously stirred. This causes crystallisation to begin with the evolution of heat, and the deposition of the nitrate in granular translucent lumps, having the composition  $\text{Th}(\text{NO}_3)_4 + 4\text{H}_2\text{O}$ . It is in this form that the nitrate is sometimes sold to incandescent mantle manufacturers, but more usually 1 to 2 per cent. of sulphuric acid is added to the solution just before crystallisation, as the addition of this substance causes the ash, left on ignition of the nitrate, to be soft and voluminous. By allowing the acid solution of the nitrate to crystallise slowly, clear tabular crystals are obtained which have the composition  $\text{Th}(\text{NO}_3)_4 + 12\text{H}_2\text{O}$ .

Various processes have been patented for the direct separation of thorium from the cerium earths without fractional crystallisation, but no information is available as to whether any of these are in use on a large scale.

According to recent descriptions, one of the most promising methods appears to be the use of hypophosphate of sodium (see United States Patent, 1,069,959 of 1913, M. Koss, *Chem. Zeit.*, 1912, 36, 686; A. Rosenheim, *Chem. Zeit.*, 1912, 36, 812; F. Wirth, *Zeits. angew. Chem.*, 1912, 25, 1678). This reagent is stated to precipitate thorium quantitatively from acid solution, whilst the other rare earths remain in solution. At the present time, however, the reagent is too expensive for use on a commercial scale in competition with the methods of fractional precipitation.

Sodium pyrophosphate is stated to act in a similar manner (see R. J. Carney and E. D. Campbell, *Journ. Amer. Chem. Soc.*, 1914, 36, 1134).

The use of sebacic acid has also been patented (German Patent, 266,459, 1912).

From 80 to 90 per cent. of the thorium present in monazite is recovered by the present-day methods of separation, the efficiency of the recovery usually increasing with the scale on which the operations are conducted.

**The Recovery of Thoria from Waste Mantle Ash.**—In some countries waste mantle ash, derived from factory trimmings and used mantles, forms a small but important source of thoria. Numerous processes have been devised for extracting the thoria from the ash and converting it to the nitrate. In one of these the crude ash is first sieved, in order to remove as much as possible of the asbestos fibre used for attaching the mantle to its support. The sieved ash is next treated, for some hours, with twice its weight of hot concentrated sulphuric acid; the pasty mass, after cooling, is poured into cold water and the rare earths precipitated by the addition of ammonium oxalate. The rare earth oxalates are then converted to the nitrates by one of the well-known processes.

The cost of manufacture of thorium nitrate from monazite varies, to some extent, with the price of the raw material, but, in the past, it would appear that the price has been regulated by the syndicate which controlled the output of raw monazite from Brazil. According to C. R. Böhm, if monazite containing 5 per cent. of thoria is sold at £30 per ton, *i.e.*, £6 per unit of thoria, then thorium nitrate can be produced at 16s. to 17s. per kilo. Another estimate by E. White puts the *works* cost of production at 10s. to 12s. per kilo, when the raw monazite is sold at about £4 per unit of thoria. The amount of monazite required to produce one kilo of technical thorium nitrate costs between 4s. and 5s., if the raw material is bought on a basis of £4 per unit of thoria.

In the past the price of thorium nitrate has been subject to wide variations, as is shown by the following table giving price per kilo :—

1894	- £100	0	0	1907	£1	14	0
1898	2	0	0	1908	1	5	0
1900	1	14	0	1909	0	18	0
1904	2	3	0	1910	0	19	0
1906	1	7	0	1912	0	18	0

At the present time (June 1914), technical thorium nitrate costs about 18s. per kilo, in the United Kingdom.

### Testing of Thorium Nitrate for Mantle Manufacture

The following is a brief summary of the tests which the salt is usually required to pass in order to satisfy the requirements of mantle manufacturers :—

**Solubility and Colour.**—When 25 gm. of the nitrate is stirred with 25 c.c. of distilled water, for 10 minutes, it should be completely soluble, and the solution should have only a slight yellow colour.

**Ignition.**—The nitrate, after ignition in a platinum crucible for thirty minutes, in a blast flame, should leave a residue of not less than 48 per cent. The ash should be quite white and free from any pinkish or yellowish tint.

**Cerium.**—Dissolve 2 gm. in 10 c.c. of distilled water, and add sufficient potassium carbonate solution to dissolve the precipitate first formed. The addition of a few drops of hydrogen peroxide to this solution should not give any appreciable yellow colour. This test will indicate 0.004 gm. of cerium oxide.

**Didymium.**—The ash produced by the above ignition is suspended by a platinum wire for two minutes in the flame of a Bunsen burner. After cooling and crushing, the ash will be pink if didymium oxide is present. This test is very sensitive. The yellow colour imparted to the flame in this test should be only transient, and the ash should show practically no luminosity in the ordinary (not blast) Bunsen flame. The presence of almost any inorganic impurity will cause the ash to become luminous.

**Iron and the Heavy Metals.**—Only a slight coloration should be produced on mixing a 30 per cent. solution of the nitrate with an equal volume of a 2 per cent. solution of ammonium thiocyanate. To test for the heavy metals, 20 c.c. of a 30 per cent. solution is mixed with 50 c.c. of water saturated with sulphuretted hydrogen. At the most, only a slight darkening should be produced, without any trace of a permanent precipitate.

**Phosphoric Acid.**—The nitrate should not contain more than 0.004 per cent. of  $P_2O_5$ . For the quantitative determination of this constituent about 25 gm. of the sample is taken, and the phosphate is precipitated in the usual way with ammonium molybdate in acid solution.

**Sulphuric Acid.**—The determination of sulphate in the presence of thorium nitrate by the usual method of precipitation with barium chloride gives low results. E. White recommends fusing the nitrate with four times its weight of solid potassium hydroxide, extracting the mass with water, and after filtering off the insoluble matter, determining the sulphate in the filtrate in the usual manner. Another process is to dissolve 10 gm. of the nitrate in 250 c.c. of distilled water and add 5 c.c. of hydrochloric acid and 5 gm. of oxalic acid. After allowing to stand for some hours, an aliquot part of the clear liquid is filtered off and the sulphate estimated in the usual manner.

Makers of mantles usually require a nitrate which, on ignition, shall leave a soft voluminous ash, and for this purpose sulphuric acid is added to the nitrate before crystallisation, so that the finished nitrate contains about 2 per cent. of sulphate. Thorium nitrate free from sulphate leaves, on ignition, a hard dense ash unsuitable for mantle manufacture by the ordinary process.

**Aluminium, Calcium, Magnesium, and Sodium,** together with the iron and phosphoric acid, are determined by precipitating the rare earths with oxalic acid, evaporating the filtrate to dryness, and weighing the residue remaining after ignition, which should not amount to more than 0.05 per cent. of the original thorium nitrate.

**Influence of Impurities.**—Alkalies and alkaline earths in the body of the mantles cause them to shrink and lose their shape. Phosphates cause excessive brittleness, whilst didymium and lanthanum produce a decrease in luminosity. Traces of iron and the heavy metals have but little effect, as they are largely volatilised during the ignition of the mantle.

## The Manufacture of Incandescent Gas Mantles

This industry, which has now attained such an enormous size, may be said to have started in 1884, when Welsbach patented the use as a lighting medium of a fibrous network composed of the oxides of certain of the rare elements (French Patent, No. 172,064 of 1884; German Patent, 39,162, Class 26 of 1885).

The first mantles were made of the oxides of zirconia, lanthana, and yttria (English Patent, 3,592 of 1886), but were not a success, as they could not stand any shock and had very inferior lighting power. The next advance was in the employment of thoria, either alone or mixed with other oxides (English Patent, 15,286 of 1886).

The incandescent mantle cannot be said to have been a commercial success until 1893, when Welsbach patented the use of a mixture containing 98 to 99 per cent. of thorium oxide, together with 1 to 2 per cent. of cerium oxide (English Patent, 124 of 1893). In these proportions the oxides have their maximum light-giving power. Later investigations have shown that pure thoria has little light-emitting power, and that the addition of over 2 per cent. of ceria causes a decrease in luminosity of the mantle, until about 10 per cent. is reached, when the light falls to about the same quantity as is emitted by pure thoria. The changes caused in the intensity of the light emitted by incandescent thoria, by the

addition of varying amounts of ceria, is well illustrated in Fig. 5. This curve has been drawn from the results of G. P. Drossbach (*Journ. für Gasbel*, 1898, **41**, 352; see also J. Lux, *Zeits. für Beleuchtung*, 1907, 246). From the year 1893 up to the present time, many oxides have been tried in place of these, but none have, thus far, been found to be so efficient.

In the conversion by ignition of thorium nitrate to the oxide, thoria, the material expands so that it occupies at least ten times its original volume. As the cerium nitrate does not appreciably change its volume when converted to the oxide, in the mantle the volume ratio of the thorium oxide to cerium oxide is 999 to 1. According to the work of A. H. White and H. F. Travers (*Journ. Soc. Chem. Ind.*, 1902, **21**, 1012), 100 parts of thoria can hold 6.7 parts of cerium

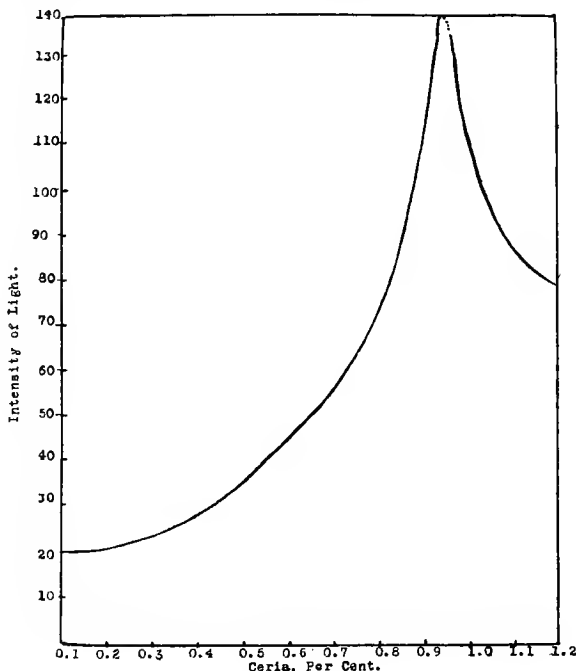


FIG. 5.

oxide ( $\text{Ce}_2\text{O}_3$ ) in solid solution, and, therefore, all the cerium in the incandescent mantle is in the dissolved condition.

It is impossible to give a full account of this important branch of technology in the space available, but the following is a brief outline of the more important parts of the process.

**Fabric.**—The earlier mantles were made of **cotton**, but as these were found to give a decreased illumination after being in use for a short time, this material has been largely supplanted by **ramie** fibre for the better quality goods. Recently, **artificial silk** has been used with satisfactory results, as it combines the high and well-maintained illuminating power of ramie with a greater elasticity of the ash skeleton, and the mantles produced are, therefore, more capable of withstanding shock. German makers are largely using cuprammonium cellulose and Chardonnet silks, whilst the French makers prefer to use “viscose” silk (see English Patent, 8,700, 1892), which is also used in this country. Artificial silk mantles have the additional advantage that they do not require washing before impregnation.



The appearance of impregnated fibres, made of the three classes of materials mentioned above, both before and after "burning off," is well illustrated in the



FIG. 6.—Cotton before Burning Off.

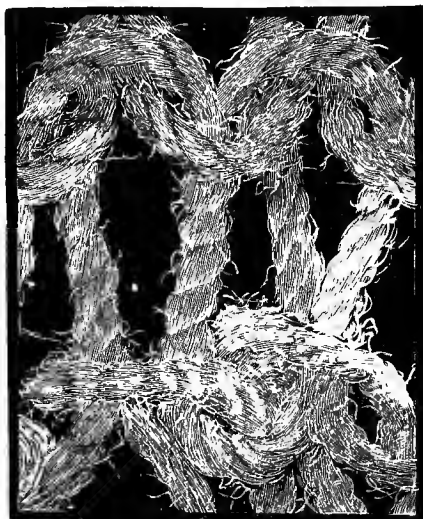


FIG. 7.—Cotton after Burning Off.

*Reproduced by permission from Thorpe's "Dictionary of Applied Chemistry."*

photo-micrographs shown in Figs. 6 to 11. Cotton fibre (Figs. 6 and 7) is seen to have a very twisted structure, whilst that of ramie (Figs. 8 and 9) is of a somewhat simpler form. The structure of artificial silk is very similar to that shown in Figs. 10 and 11, which show collodion fibres impregnated with thorium nitrate.



FIG. 8.—Ramie before Burning Off.

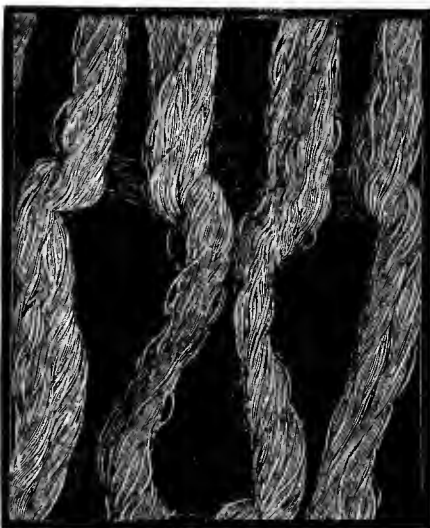


FIG. 9.—Ramie after Burning Off.

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The yarn used in the manufacture of incandescent mantles is tested, at the works, both as regards its "count" and breaking strain: the latter is of importance on account of the tension which the yarn has to undergo during knitting of the "stocking." The efficiency of the mantle varies directly, within certain limits, as the tension to which it is subjected during knitting.



FIG. 10.—Collodion before Burning Off

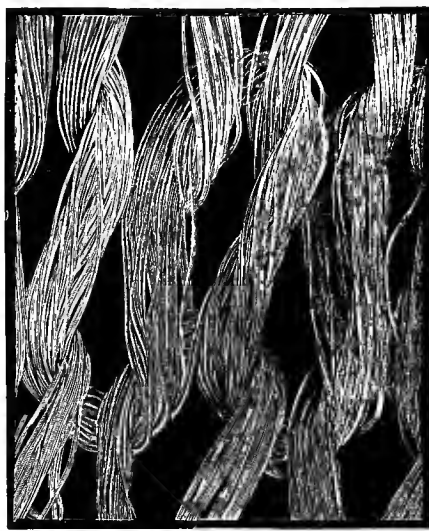


FIG. 11.—Collodion after Burning Off.

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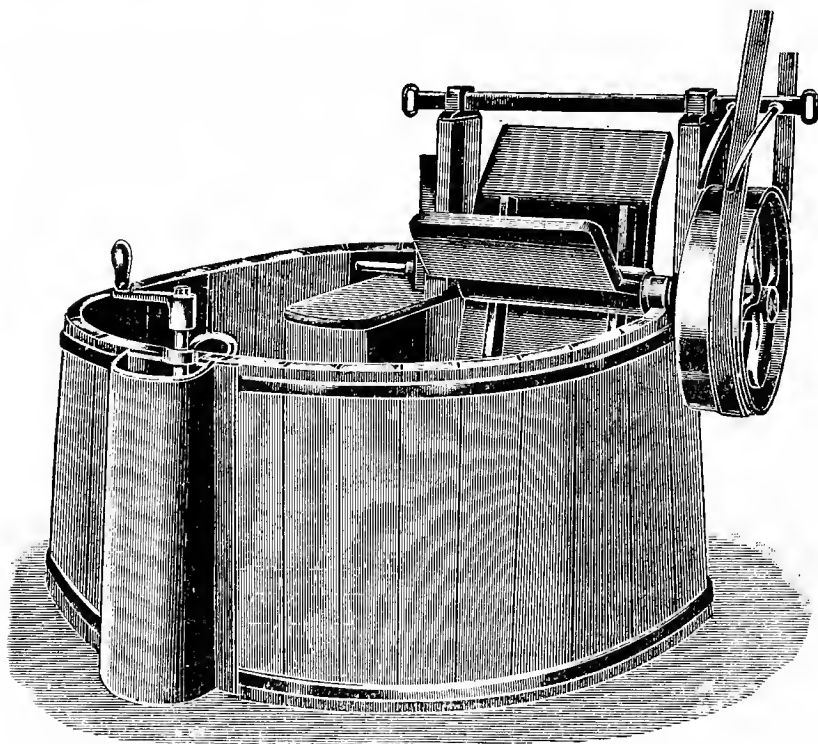


FIG. 12.—Washing Machine.

**Washing.**—Before being impregnated with the solution of the rare earths, the web for cotton and ramie mantles needs to be washed in order to decrease the quantity of mineral matter, and also to remove any fatty substance present. Ramie mantles are soaked overnight in a 2 per cent. solution of nitric acid, and next morning, after the superfluous liquid has been removed by means of a centrifuge, they are well washed in distilled water, and treated with dilute ammonia, and then again thoroughly washed with distilled water. Cotton mantles are washed, first in a 3 to 5 per cent. solution of caustic soda, and next in a 1 to 3 per cent. solution of hydrochloric acid. The alkaline bath is usually employed warm. The above methods are all subject to variation, according to the individual ideas of the manufacturer. A washing machine is shown in Fig. 12. By the above treatment the ash content of the mantle before impregnation is reduced to about 0.02 per cent., and consists largely of iron oxide and silica. Reduction of the ash below 0.01 per cent. is stated to be detrimental to the strength of the ash skeleton. Each batch of washed material should have its ash content determined. In all the following operations great cleanliness is necessary.

**Drying.**—This is done by suspending the mantle, in a current of hot air, in a special drying apparatus which may consist of a chamber in which the web is

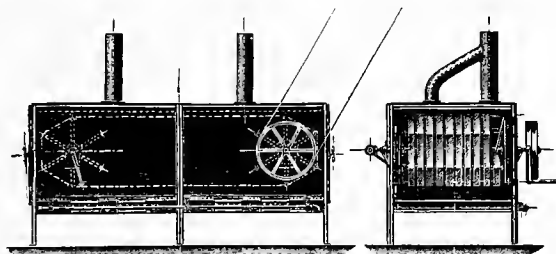


FIG. 13.—Drying Chamber.

suspended on poles, or of a special drying box round the inside of which the web passes a number of times. A machine of the latter type is illustrated in Fig. 13.

**Impregnation.**—For this purpose a solution containing from 25 to 50 per cent. of thorium and cerium nitrates is used, the proportions employed being about 99 per cent. of thorium salt to 1 per cent. of cerium. Small quantities of beryllium or magnesium nitrate are also added to strengthen the ash skeleton.

The composition of certain solutions used for impregnating is shown in the following table :—

TABLE VIII.

	1.	2.	3.	4.	5.
	Grams.	Grams.	Grams.	Grams.	Grams.
Thorium nitrate (48-49 per cent. $\text{ThO}_2$ )	1,000	1,000	1,000	1,000	1,000
Cerium nitrate	10	8	10	10	10
Beryllium nitrate	5	2	5	5	...
Magnesium nitrate	1.5	1.5	2.5	2	1
Distilled water	2,000	2,400	1,800	1,600	2,500

Many makers adjust the impregnating solution so that inverted mantles, after ignition, contain 0.5 to 0.8 per cent. of ceria, whilst the upright type contain 1.0 per cent.

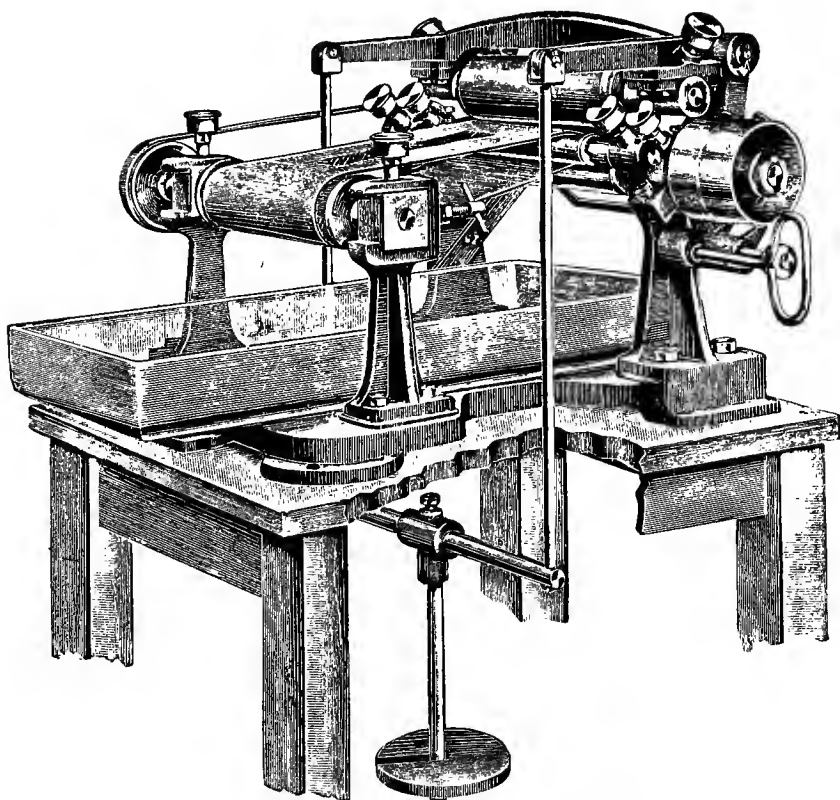


FIG. 14.—Impregnating Machine,  $\frac{1}{10}$  Actual Size.

Formulæ for ramie mantles are given in columns 1 to 4, the latter being a stronger solution for impregnating mantles intended for use with high-pressure gas; No. 5 is for cotton mantles. Beryllium nitrate is sometimes added to the solution used for impregnating cotton mantles, if these have to be given special shapes such as those used in pressure or petrol gas lighting. The time of impregnation varies from about two minutes, in the case of cotton and ramie mantles, to about five hours in the case of certain artificial silk mantles. If the quantity of magnesium nitrate in the impregnating solution is much increased over that shown above, the time required for "burning off" is considerably reduced, and hence the cost of production is slightly lowered. After impregnation, superfluous liquid is removed by passing the ramie and cotton mantles through a wringing machine, the rollers of which can be adjusted so as to regulate the quantity of solution left in the mantle, and hence its final weight after "burning off." Such a machine is illustrated in Fig. 14. The artificial silk mantles have their superfluous solution removed by means of a centrifuge.

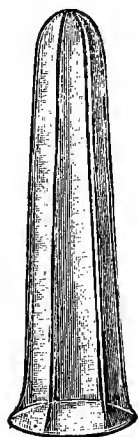


FIG. 15.—Glass Drying Cylinder.

The mantles are next dried at a temperature of about 30° C., those of ramie and cotton, which are cut up into lengths before impregnation, being stretched on glass cylinders (Fig. 15), whilst the silk ones are treated in lengths on wooden rollers. The cheaper grades are, however, usually cut up after impregnation and drying.

The upright mantles are next fitted with a sewn-on tulle head, together with the asbestos loop, by which they are suspended, unless these were attached before impregnation. Inverted mantles are drawn together with impregnated cotton to form the "spider," and are fixed to the supporting ring (see p. 25).

**Fixing.**—The mantle also requires to have strengthened those parts which, when in use, will be subjected to the greatest strain: these are the head and loop of upright and the portion around the ring of inverted mantles. The method sometimes used is to treat these portions with a thorium solution containing a much larger proportion of salts of calcium, aluminium, or magnesium, than that employed for impregnating. On "burning off" (see below), the portions of the mantle so treated shrink more than the body, and so become more compact and therefore stronger. The solution may contain aluminium nitrate, 20 parts; magnesium nitrate, 20 parts; borax, 0.3 parts; water, 100 parts.

A machine for applying this "fixing" liquid is shown in Fig. 16. In this a felt pad saturated with the fixing solution is pressed against the dried impregnated mantle whilst the latter is slowly rotated. A small quantity of methyl blue is often added to the solution in order to show where it has been applied. In many works it is now customary to apply the fixing solution by means of a spraying machine working on the "Aerograph" principle. Upright mantles are usually fixed before the tulle head is sewn on.

**Branding.**—If it is desired to brand the mantle with a trade mark or maker's name the design is stamped upon it with a solution consisting of:—

Didymium nitrate	-	-	1,000 gm.
Glycerine	-	-	200 "
Methyl blue	-	-	25 "
Alcohol (96 per cent.)	-	-	300 "
Distilled water	-	-	500 "

This solution gives a brand which can be readily seen both before and after "burning off." Although upright mantles are usually branded after fixing, it is more customary to brand the inverted type before mounting them on the ring.

**Burning Off.**—The mantle is next shaped on a wooden model and burnt off from the top with a Bunsen flame. Formerly, this operation, together with those of "shaping" and "hardening," was performed by hand, but it is now the general custom to use a machine similar to that illustrated in Fig. 17, which is designed for inverted mantles. It consists, essentially, of two rows of gas burners mounted on an iron frame, with a mechanical arrangement for raising or lowering the burners and gas pressure, and a removable bar with clips from which the mantles are

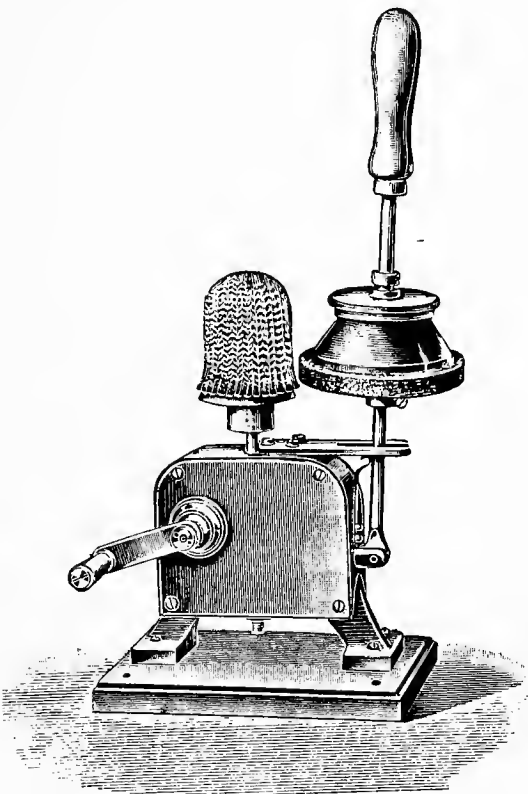


FIG. 16.—Machine for Applying "Fixing" Solution to Inverted Mantles,  $\frac{1}{3}$  Actual Size.

suspended. The machine is also furnished with a movable screen of blue glass in order to protect the operator from the heat and intense light. The upper row of burners, to which the gas is delivered at a pressure of two to four inches of water, are for carbonising the mantle; the lower row, which are fed with a mixture of gas and air under pressure, being for "hardening" the ash skeleton by subjecting it to a more intense heat. The "burning off" is always begun from the *top* of the mantle, for if the operation is performed in the reverse order the mantle will probably be so mis-shapen as to be quite useless. As soon as the carbonisation

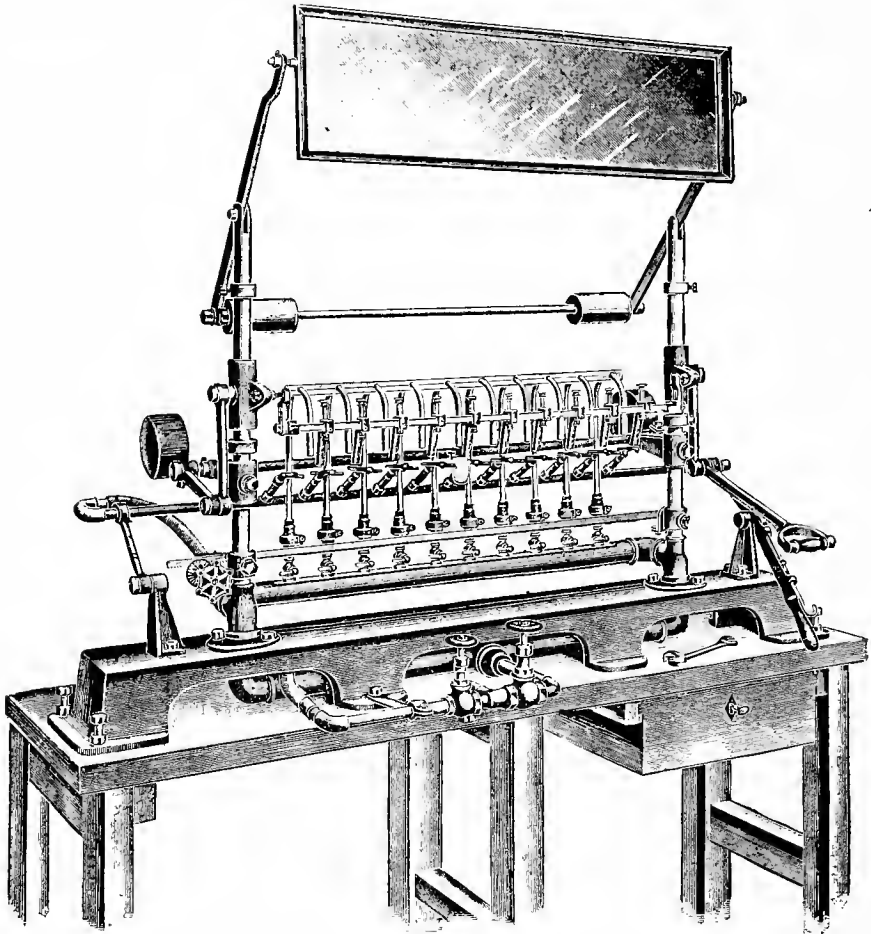


FIG. 17.—Burning Off and Hardening Machine for Inverted Mantles,  $\frac{1}{14}$  Actual Size.

of the mantle is complete, it is "shaped" by being heated from top to bottom by one of the low-pressure burners. It is next "hardened" by being heated in one of the high-pressure burners, the operation lasting from  $1\frac{1}{2}$  to 15 minutes according to the size of the mantle.

In another type of machine the inverted mantles are supported by the lugs of their fireclay rings, which just rest above holes in metallic saucers, which are suspended over the burners of a machine very similar to that described above.

During the process of "burning off" a considerable shrinkage takes place in the size of the mantle, the ratio between the size before and after the operation

being dependent upon a number of factors, such as count of yarn, stitch used, tension of knitting, heaviness of impregnation, etc. The following figures may serve as an illustration—"ramie stocking" for a "C" size upright mantle 20 cm. long and 10 to 14 cm. in circumference will give a mantle about 10 to 14 cm. long and 9 cm. in circumference.

The number of mantles which can be made from 1 kilo. of thorium nitrate varies with the size and quality of the mantle; for "C" size upright mantles the number made per kilo. by a well-known works are as follows:—Best quality, 500 to 600; medium quality, 700 to 800; cheap quality, 1,000. As many as 1,200 mantles of the cheap German type may be produced from 1 kilo. of thorium nitrate.

**Collodionising.**—The mantles, which now consist of an ash skeleton, are

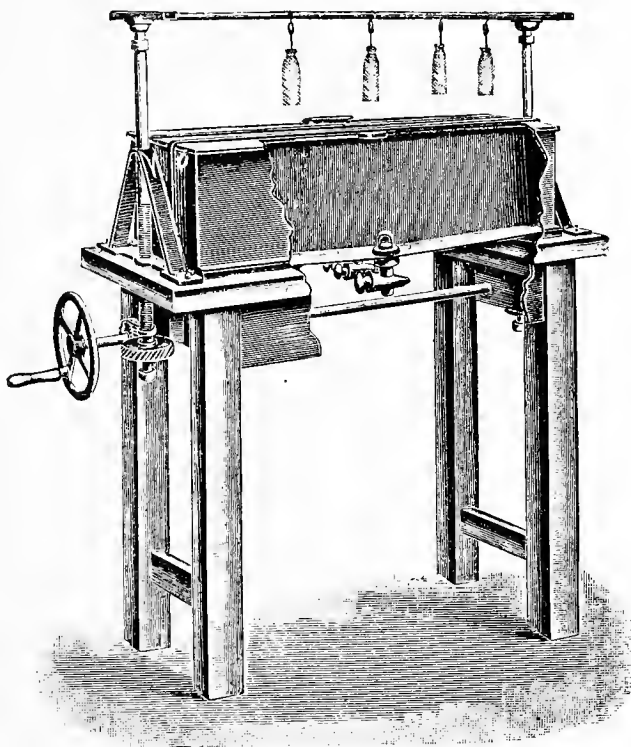


FIG. 18.—Collodionising Bath,  $\frac{1}{10}$  Actual Size.

made suitable to bear transport by being immersed in a solution somewhat of the following composition:—

Collodion solution (4 per cent.) -	-	-	-	100 parts
Ether -	-	-	-	40 „
Camphor -	-	-	-	6.5 „
Castor oil -	-	-	-	3.5 „

The mantle, after collodionising, is still somewhat fragile, and any blows which it receives will probably show as cracks when the mantle is brought into use. To overcome this defect, certain makers add inorganic salts such as the nitrates of thorium, zirconium, or beryllium to the collodion solution.

This operation is carried out by means of a machine, the principle of which is illustrated in Fig. 18. It is customary, however, in most large works to perform

the operation on a much larger scale in a closed room which has special arrangements for the condensation and collection of the volatile vapours evolved.

After drying at a temperature of  $50^{\circ}$  to  $60^{\circ}$  C. the mantles are trimmed (see Fig. 20) and are ready for use. It is desirable that this drying should be performed fairly rapidly, as slow drying may cause undue strain to the mantle.

The manufacture of **incandescent mantles** from **artificial silk** is usually carried out in a manner differing somewhat from that already described for ramie or cotton. When nitro-cellulose is used, the impregnated fibre has to be denitrated before "burning off," otherwise the combustion would be so rapid as to destroy the form of the mantle. This denitration is unnecessary if "viscose" silk be used. One process may be quoted as an example of the method of procedure if nitro-cellulose is used (French Patent, 462,156, 1911). The silk, after being freed from grease by washing in ether containing a little carbon disulphide, is impregnated in a thorium-cerium nitrate bath of the usual strength. After drying, the impregnated fabric is denitrated by immersing it in 95 per cent. alcohol, to which has been added a little hydrofluoric acid. This treatment causes the thorium to be precipitated in an insoluble and viscous condition in the fabric, which is next washed in distilled water, and finished in the same manner as are ramie mantles.

Many patents have been granted for processes for the conversion of the thorium nitrate to an insoluble form whilst in the fabric, by means of a precipitant. The object of this precipitation is to obtain the thorium in a very dense form, so that on ignition it will give a more coherent ash skeleton than is obtained from the nitrate.

Substances for this purpose include ammonia (English Patent, 20,747, 1901; 11,042, 1902; and French Patent, 321,803, 1902), hydrogen peroxide (French Patent, 438,260, 1911), ozone (French Patent, 414,700, 1909), and aqueous solutions of amines mixed with a suitable acid or phenol (French Patent, 403,443, 1909).

This increase in strength of the ash skeleton is a matter of considerable importance for mantles which will be subjected to much vibration, such as those used for railway carriage lighting.

Of course, when this is desired, the thorium nitrate used for impregnation does not contain any sulphate (see p. 15), which causes the material to swell up enormously on ignition.

The increased use of pressure gas and vapourised oil for incandescent lighting has also led to a demand for extra strong mantles of this type, which are particularly necessary for use with certain incandescent oil burners in which the gaseous product is often delivered from the jets at a pressure of about 25 lbs. to the square inch. According to information supplied by a manufacturer in the United Kingdom who specialises in the production of mantles for the lighting of railway carriages, the most satisfactory material for this purpose is "viscose" silk (for an account of artificial silks see G. Martin, "Industrial Chemistry," vol. i., p. 214).

The following is a very brief description of one process of manufacture employed (English Patent, 25,549, 1908). The fabric, if "viscose" silk be used, is impregnated in the usual manner, almost completely dried, and placed in a vacuum chamber in order to remove all occluded air and moisture. When this has been satisfactorily accomplished, dry gaseous ammonia is slowly admitted to the chamber, thus causing a more complete precipitation of the thorium than

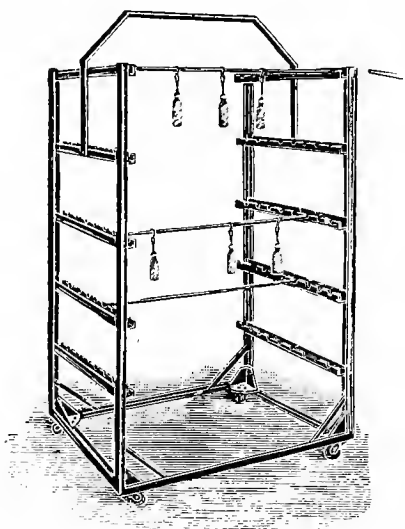


FIG. 19.—Movable Drying Crate for 500 Mantles,  $\frac{1}{2}$  Actual Size.



could be obtained by immersion in aqueous ammonia, even when this latter treatment is preceded by evacuation. When the precipitation is considered to be complete, the ammonia is slowly blown out by a current of air, the mantles removed, washed, and finished in the usual manner. It is claimed that the tensile strength of mantles prepared in this way is greater than those of equal illuminating power prepared by the ordinary process. When cotton or ramie is employed in this process, in place of artificial silk, the fabric before impregnation is steamed, so as to open the fibres, placed in a vacuum, and the thorium solution slowly admitted.

Artificial silk mantles usually have the "burning off," shaping, and "hardening" performed in one operation. Owing to the fact that the individual threads of

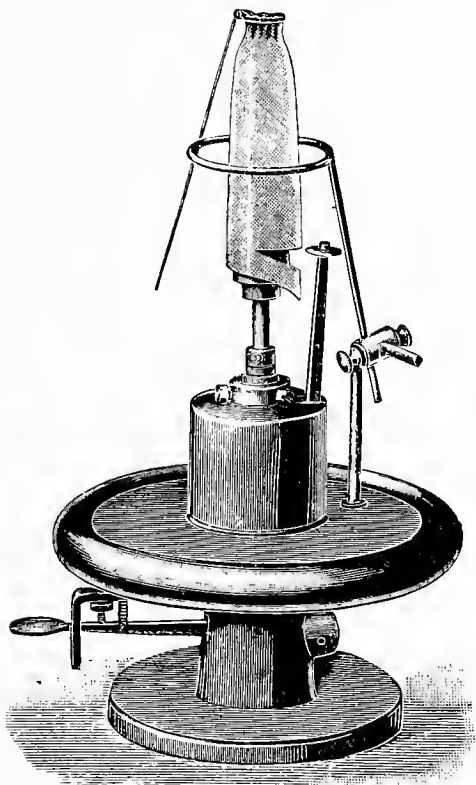


FIG. 20. —Machine for Trimming Upright Mantles,  $\frac{1}{4}$  Actual Size.

mantles of this type have a tendency to contract and become entangled when carbonised, a special arrangement is necessary for "burning off." The mantles are suspended over a guiding tube, the outer diameter of which is equal to that desired for the finished mantle, so that only the head is above the top of the burner, which passes through the inside of the guiding tube. The mantle is ignited and slowly moved upwards until only the bottom is in contact with the flame. Artificial silk mantles for high-pressure lighting are often sent out from the works in the soft unburnt condition.

A general review of the use of artificial silk for incandescent mantle manufacture is given by F. Wirth (*Chem. Zeit.*, 1911, 35, 752).

The manufacture of the **rods** and **rings** for supporting upright and inverted mantles, respectively, is an important matter in this branch of technology, but one which cannot be considered fully here. These articles are usually not made on

the mantle works. A description of their manufacture is given by C. R. Böhm ("Die Fabrikation der Glühkörper für Gasglühlicht"), and a recent account of comparative experiments with porcelain mixtures and alundum is given by R. L. Clare (*Trans. Amer. Ceram. Soc.*, 1912, **14**, 407).

**Testing of Gas Mantles.**—The testing departments of certain public bodies have instituted a series of tests for the comparison of the various mantles on the market as regards their durability and lighting properties.

The **durability** is determined by means of the **Woodall-Moon** or similar machine (see Fig. 21), in which a mantle is fixed to its burner, and after being burned off for about five minutes is subjected to a series of shocks administered by a miniature stamp driven by a water motor. The shocks given to the mantle can be varied by altering the weights used to load the rod which causes the shock, and the vibrations thus produced are stated to be similar to those occurring when heavy traffic passes along a road. According to a recent article by J. H. Coste and W. E. F. Powney (*Journ. Soc. Chem. Ind.*, 1911, **30**, 65) the usual test which upright mantles are required to stand, without fracture, is 1,000 shocks administered at the rate of 300 per minute, using 2 oz. weights. For inverted mantles the test is 3,000 shocks at the rate of 600 per minute, using 3 oz. weights. In both cases the Woodall-Moon machine is used.

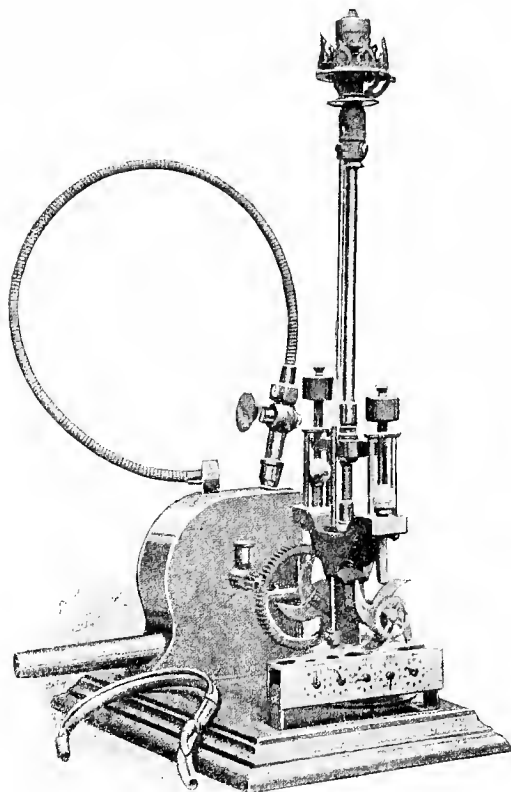


FIG. 21.—Woodall-Moon Mantle Tester.

The illuminating power of the mantles is tested by means of one of the well-known types of photometers.

**Statistics of Production.**—Accurate figures cannot be obtained, but the annual consumption of incandescent mantles in 1912 was estimated to be approximately as follows:—

	Millions.
Germany - - - - -	100
United States - - - - -	60
United Kingdom - - - - -	38
France - - - - -	16
Belgium - - - - -	3.5
Italy - - - - -	3.0
Russia - - - - -	1.5

222.0

A recent estimate places the total consumption of incandescent mantles at 300 millions per annum.

Although rapid advances have been made in the manufacture of incandescent mantles in this country, there are still enormous numbers imported from Germany. Complete statistics are not available, but the value of the incandescent mantles imported into and exported from the United Kingdom and the United States are shown in the following table:—

TABLE IX.

	1911.	1912.	1913.
IMPORTS.			
	£	£	£
United Kingdom	277,357	322,631	302,576
United States	13,331	13,555	12,785
EXPORTS.			
United Kingdom (home manufacture)	28,126	40,728	32,566
United Kingdom (foreign manufacture)	15,412	3,274	5,650
United States	<i>Nil</i>	<i>Nil</i>	<i>Nil</i>

### Minor Uses of Thorium Compounds

Small “pastilles,” consisting largely of thoria, together with a trace of ceria, are finding an extensive use for lighting of the “limelight” type, such as is used in searchlights and for the headlights of motor cars.

The use of certain thorium compounds as constituents of magnesium **flashlight powders** has been patented. Thus, the use of thorium chromate or tungstate is covered by French Patent, 14,692, 1908, whilst certain other salts are mentioned in English Patent, 27,267, 1904, and French Patent, 403,722, 1909. The chief claims made for these powders is that they evolve considerably less smoke, when fired, than do those consisting of magnesium alone.

A method for preparing **colloidal thorium** is given on p. 85, and the use of the metal in filaments for incandescent electric glow lamps is described on p. 84.

### PATENT LITERATURE

Since its introduction, numerous patents have been taken out covering many improvements in the manufacture of the incandescent mantle. In the following list are included the more important patents granted in the United Kingdom. An attempt has been made to classify these according to the nature of the improvement claimed; unfortunately, this has not been possible in all cases. Short abstracts of the majority of these specifications will be found in the *Journal of the Society of Chemical Industry*.

**Weaving and Knitting the Web.**—English Patents, Nos. 3,323, 3,530, 5,821, 13,259, 16,473 of 1900.

**Composition and Treatment of Fabric before Impregnation.**—English Patents, Nos. 11,038, 15,246 of 1895; 13,256, 26,304, 29,613 of 1896; 26,381 of 1897; 3,770 of 1898; 63, 11,653 of 1899; 9,088, 19,859 of 1900; 454, 9,551, 20,747 of 1901; 17,603, 20,004 of 1902; 25,698 of 1903; 7,668 of 1904; 24,680 of 1905; 18,152 of 1906; 3,055 of 1908; 21,315 of 1911.

**Impregnating Solutions.**—(1) *With a Thorium Salt as the Chief Constituent.*—English Patents, Nos. 10,129, 19,202 of 1895; 1,681, 1,682, 2,000, 3,262, 3,681, 9,244, 13,659, 14,365, 14,448, 21,267, 26,167, 27,269 of 1896; 501, 11,739, 14,499, 15,963, 20,225, 26,202, 29,767, 30,145 of 1897; 2,015, 13,504, 14,184, 14,259, 15,713 of 1898; 8,058 of 1899, 5,989 of 1900; 827, 4,229, 12,137 of 1901; 21,861 of 1902; 16,018 of 1905; 6,828 of 1907; 422,643 of 1910; 17,492 of 1911; 25,360 of 1912.

(2) *Containing no Thorium Salt.*—5,646 of 1883; 17,866 of 1888; 4,732, 7,372, 10,427, 20,735 of 1894; 24,505 of 1895; 1,841, 4,000, 14,845, 15,500, 17,194 of 1896; 3,811, 14,499; 20,221, 30,112 of 1897; 49, 25,653 of 1898; 9,273, 16,166 of 1899; 3,925 of 1900; 1,629 of 1909.

**Precipitation of Thoria in Fabric.**—English Patents, 16,053 of 1899; 20,747 of 1901; 11,042 of 1902; 14,288 of 1904; 15,295 of 1906; 16,867 of 1907; 10,233 of 1908; 10,400, 23,434 of 1909; 11,904, 13,169, 27,837 of 1911.

**Strengthening the Mantle.**—English Patents, Nos. 7,330, 22,327 of 1897; 20,740 of 1898; 13,181 of 1906; 25,657 of 1907; 27,755 of 1908.

**Indestructible Mantles.**—English Patents, Nos. 8,162 of 1905; 3,785, 28,435 of 1908.

**Stamping Trade Marks on Mantles.**—English Patents, Nos. 1,538 and 12,077 of 1899.

**Self-Lighting Mantles.**—English Patents, Nos. 16,966, 26,618 of 1896; 15,414, 17,575, 20,017, 25,268 of 1898; 23,701 of 1900; 609 of 1903; 19,435 of 1905; 255, 18,602 of 1906.

**Colloidionising and Rendering Suitable for Transport.**—English Patents, Nos. 23,986 of 1902; 15,696 of 1903; 6,814 of 1909; 15,536 of 1907; 2,572 of 1908; 4,860 of 1909; 11,459 of 1910.

**Machinery for "Burning Off," etc.**—English Patents, No. 25,171 of 1899; 4,302, 6,952, 12,413, 17,637, 24,218 of 1901; 24,032 of 1904; 6,432 of 1905; 6,556, 12,579 of 1907.

**Miscellaneous Patents.**—English Patents, Nos. 3,592, 9,806, 11,287, 16,581 of 1886; 6,236, 1,195 of 1887; 22,396 of 1893; 18,309 of 1894; 811, 4,324 of 1895; 6,919, 12,950, 18,800 of 1899; 4,707, 9,466, 9,733 of 1901; 11,042 of 1902; 14,687 of 1905; 6,814 of 1906; 2,240 of 1908; 27,354 of 1911; 19,668 of 1912.

A list of the patents granted in Europe and the United States, complete to 1902, is given by C. R. Böhm in "Das Gasglühlicht."

## CERIUM, LANTHANUM, AND DIDYMIUM

The oxides of these elements are important constituents of many minerals, such as **monazite**, **cerite**, **allanite**, and **gadolinite**, but at the present time, owing to the large quantity of cerium earths which are available as by-products in the manufacture of thorium nitrate, none of these minerals are utilised solely as a source of the oxides (see p. 11).

For many years there was no commercial outlet for the large quantities of rare earths thus obtained, which amount to about twelve times the quantity of thoria produced, and constitute 65 per cent. of the raw monazite, and hence thousands of tons remained on the works unutilised. It is true that the incandescent mantles contain about 1 per cent. of cerium oxide, but this only consumes a small fraction of the total amount available.

These rare earths, other than thoria, obtained from monazite, consist of about 45 per cent. cerium sesquioxide, 25 per cent. lanthanum oxide, 15 per cent. neodymium oxide, whilst oxides of yttrium and samarium constitute the remainder.

The following is a brief account of some of the uses to which these oxides have been put recently.

**Pyrophoric Alloys.**—In 1903, Auer von Welsbach, when conducting an investigation of the properties of the alloys obtained by reducing this mixture of rare earth oxides, found that, when filed, certain of these gave off a shower of bright sparks, which were sufficient to ignite inflammable gas. This discovery was patented (German Patent, 154,807, 1903, and English Patent, 16,853, 1903), and he disposed of his rights, to a German company, for the sum of £30,000, and so started the pyrophoric alloy industry. At a later date, he found that this property was largely due to a superficial layer of oxide, which needed frequent renewal if the alloy was to retain its pyrophoric properties, and numerous patents were taken out covering methods for the production of this oxide layer (see English Patent, 8,163, 1909; French Patent, 407,117, 1909).

The necessity for these renewals has since been obviated by the discovery that alloys of the cerium earth metals with certain of the heavy metals, such as iron, nickel, manganese, and cobalt, have permanent pyrophoric properties. These properties are possessed, in particular, by alloys containing from 10 to 65 per cent. of iron, and experience has shown that the best results are obtained when using 35 per cent. of iron to 65 per cent. of the cerium earth metals ("Misch" metal). Alloys of this composition, known as "**Auer**" metal, form the sparking material of a large proportion of the automatic gas and cigar lighters now on the market. Various theories have been put forward to account for the pyrophoric properties of these alloys; one is that in striking the alloy small particles of metal are broken off, and the force of the percussion is sufficient to raise these to their ignition temperature.

In the production of these alloys many difficulties have been experienced, owing to the fact that the molten "Misch" metal is extremely reactive, combining readily with oxygen, nitrogen, and hydrogen, and removing oxygen from carbon dioxide and carbon monoxide; the reduction of the rare earth oxides to the metallic

state has, therefore, to be conducted in a vacuum. The process of manufacture is briefly as follows:—

If the rare earths, which have to be converted to the anhydrous chlorides, are in the form of carbonates, they can be directly dissolved in hydrochloric acid, but if they exist in the form of oxalates, they must be converted to hydroxides and dissolved in hydrochloric acid. The complete dehydration of the chlorides, thus produced, is a matter of considerable importance, as in the later stages much depends on the suitable preparation of the material. A product containing chlorides equivalent to 35 to 50 per cent. of oxides can be easily prepared by the use of calcium chloride as the drying agent, but in order to obtain a higher grade product it is necessary to employ the ammonium chloride process in order to avoid the formation of basic salts. This process consists in heating the cerium earth chlorides with ammonium chloride until the latter is completely volatilised. This operation is too costly to be employed unless the ammonium chloride is recovered. A full account of methods suitable for the production of these anhydrous chlorides is given by A. Hirsch (*Journ. Indus. and Eng. Chem.*, 1911, 3, 880).

The preparation of the anhydrous chlorides is usually undertaken by the manufacturers of pyrophoric alloys from the rare earths remaining as a by-product in the manufacture of thorium nitrate; these can be obtained in quantity at about 6d. per kilo. The calcined chlorides cost about 3s. per kilo, and the undehydrated product can be obtained, in Germany, at about 2s. per kilo.

The dry chlorides are next electrolysed in a graphite crucible using a large iron cathode. In order to conduct the manufacture of pyrophoric alloys on a remunerative scale it is necessary to have cheap electric power, and to work with a current of not less than 1,500 amperes.

According to the patent of W. Borchers and L. Stockem (German Patent, 172,529, 1905) the chlorides are mixed in the proportions represented by the formula  $\text{CeCl}_3 + \text{CaCl}_2$ , and the addition of a small quantity of fluorspar is recommended. In another method, described in German Patent 268,827, 1912, a mixture of the anhydrous cerium earth chlorides and oxychlorides, obtained by heating the hydrous chlorides to a high temperature, is treated with alcohol, the solution separated from the insoluble residue containing the oxychloride, and the anhydrous chloride is then recovered by evaporating the alcoholic solution. Organic matter is removed by heating the anhydrous chloride in a current of dry air.

Although the electrolysis of the cerium earth fluorides has been recommended for the production of these alloys, it has not proved satisfactory on a large scale, as the molten mass obtained is so viscid that the metal produced cannot collect as a regulus, but remains scattered throughout the whole mass.

For several years past, "Auer" metal has been manufactured in the United Kingdom from cerium earths imported from Germany. "Auer" metal, at the present time (June 1914), costs about 15s. per lb. in Great Britain, and this quantity will supply the sparking material for 1,300 to 1,800 automatic lighters. Each of these small pieces, termed "firestones," will give from 2,000 to 6,000 separate ignitions.

Pyrophoric alloys are also employed in several European armies for defining the flight of shells. The friction of the air during the flight of the shell causes the alloy to burst into flame shortly after leaving the gun.

On account of its extremely reactive nature, "Misch" metal has been employed for reducing certain refractory oxides, such as those of niobium, tantalum, and zirconium.

Another pyrophoric alloy containing cerium earth metals is "**Kunheim**" metal (French Patent, No. 405,021, 1909). This consists of a mixture of hydrides of these metals, together with a certain proportion of magnesium and aluminium.

The mixture of hydrides is quite stable both in air and at a fairly high temperature, but the individual hydrides are unstable in air and lose hydrogen at a red heat. It is produced by melting the "Misch" metal with the requisite quantity of magnesium and aluminium, and then heating the alloy, thus made, in a current

of hydrogen at a temperature of about  $500^{\circ}\text{C}$ ., the operation being carried out in an electrically-heated muffle furnace. This treatment results in the conversion of a portion of the "Misch" metal into hydrides. The following is an analysis of the commercial pyrophoric alloy produced:—

	Per Cent.		Per Cent.
Cerium	36	Aluminium	1.0
Lanthanum	} 49	Iron	0.5
Didymium, etc.		Hydrogen	1.3
Magnesium	10	Silicon	0.5

For a full account of the manufacture, etc., of the above pyrophoric alloys see the work by H. Kellermann.

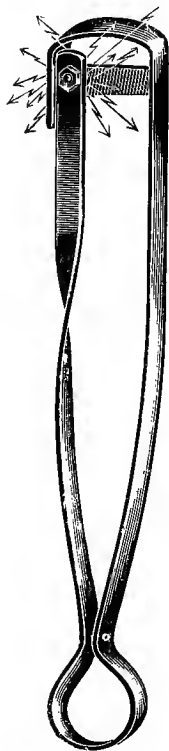


FIG. 22.

The "Whoop"  
Gas Lighter.

**Pyrophoric alloys containing "Misch" metal** alloyed with **silicon, titanium, or boron** have been patented (French Patent, 396,198, 1908, and English Patent, 27,341, 1908), and are claimed to be as efficient as the well-known ferro alloys. They can be produced by melting the metals in a magnesia crucible under a cover of sodium chloride. Pyrophoric cerium-tin alloys have been described by R. Vogel (*Zeits. anorg. Chem.*, 1911, 72, 319). The use of alloys consisting of the cerium earth metals together with one or more of the following metals:—**Cadmium, zinc, tin, or lead**, as pyrophoric substances, is covered by U.S. Patent, 1,102,575. The mixtures quoted as being suitable contain from 30 to 40 per cent. of the base metals. It is specially claimed for these alloys that they are not affected by air or moisture. A pyrophoric alloy consisting chiefly of **manganese and antimony**, together with 5 per cent. of "Misch" metal, has been patented (French Patent, No. 419,388, 1910), and is stated to be much cheaper to produce than "Auer" metal. A non-cerium pyrophoric alloy containing **titanium** is described on p. 41.

Alloys of "Misch" metal with **mercury** possess several interesting properties, but, so far, do not appear to have been put to any technical use. They can be produced (English Patent, 15,507, 1910; French Patent, 414,057, 1910) by heating the finely-divided "Misch" metal in a closed vessel with mercury vapour at a temperature of  $500^{\circ}$  to  $600^{\circ}\text{C}$ . Alloys of this type containing 10 to 16 per cent. of "Misch" metal spontaneously ignite in air, giving off bright sparks.

Typical forms of automatic lighters are shown in Figs. 22 and 23.

The general principle of all these is that a piece of hard steel, having a roughened edge, is made to strike the alloy, thus causing it to give off a shower of bright sparks which ignite an inflammable substance (gas, petrol, benzene, or tinder) placed in close proximity.

According to a recent estimate, about 200 tons per annum of the cerium earth oxides are used in the manufacture of pyrophoric alloys.

**Uses of Cerium Compounds in the Lighting Industry.**—Salts of cerium, particularly the **fluoride**, are largely employed in the preparation of electrodes for "flame arc" lighting. For certain types of electrodes the cerium fluoride is mixed with calcium fluoride, and a small quantity of sodium phosphate or borate is added in order to increase the fusibility of the mixture.

According to French Patent, No. 431,040 of 1911, the mixture may contain fluorides of the rare earths, together with compounds of the alkalis with tungsten or molybdenum. The use of a cerium pyrophoric alloy as a core for "flaming" arc carbons is covered by English Patent, No. 8,151 of 1909, whilst a mixture of the cerium earths and carbon is mentioned in English Patent, 8,151 of 1909 (see also French Patent, 414,707 of 1910).

**Cerium Titanofluoride** is also employed in this manner (English Patent, No. 13,988, 1912). In this case it has been found necessary to add sodium or potassium fluoride in order to get a steady flame. The colour imparted to the flame by these salts is corrected by the addition of a barium compound. The following is stated to be a suitable mixture for the preparation of these electrodes:

carbon 45, cerium titanofluoride 35, potassium fluoride 10, barium fluoride 10 per cent. In order to minimise the etching effect of the fluorides on the glass globes, a small percentage of either silicate, borate, tungstate, carbonate, or molybdate of sodium is added. A recent estimate places the consumption of cerium earth salts in flaming arcs at about 300 tons per annum.

**Cerium Carbide** has been tried as a filament for incandescent electric lamps (see *Electrical Engineer*, 1908, 48, 416) as also has the nitride (English Patent, 929 of 1906), but neither appear to have been satisfactory.

**Separation of Ceria from the Associated Oxides.**—Few of the preceding uses for the cerium earths necessitate the separation of any individual oxide from the mixture obtained as a by-product in the manufacture of thorium nitrate. For certain purposes, however, it is necessary to obtain cerium compounds in a state of purity, and the following are some of the more important methods which may be employed for the separation of cerium from its allies.

A process often employed is to convert the cerium earths into nitrates, and to treat the solution of these with excess of potassium permanganate in the presence of a basic substance such as sodium carbonate or magnesia (German Patent, 143,106 (see also Beyer, *Zeits. anorg. Chem.*, 1903, 37, 378, and G. P. Drossbach, *Ber.*, 1896, 29, 2,452). The process is essentially the same as that described on p. 33 for the estimation of cerium. The product obtained is quite pure, except for about 0.5 per cent. of didymium oxide.

Cerium can also be separated from the other rare earths by suspending the hydroxides in a solution of potassium hydroxide, and passing in a current of chlorine until the solution is no longer alkaline. Ceric hydroxide is formed, and remains undissolved, whilst the other rare earths are converted to soluble chlorides or hypochlorites (see P. Mengel, *Zeits. anorg. Chem.*, 1899, 19, 67).

The mixed oxides may also be dissolved in hot nitric acid, and the solution evaporated down with ammonium nitrate until ceric ammonium nitrate separates out (see Welsbach, *Monatsh.*, 1884, 5, 508, and Schottlander, *Ber.*, 1892, 25, 378).

**Cerium Nitrate** is used to a small extent in the manufacture of incandescent mantles (see pp. 16 and 19), and for this purpose it should conform to approximately the same standard of purity as that required for thorium nitrate (see p. 14).

The cerium compound obtained in a state of purity by any of the foregoing processes is converted to the hydroxide by treatment with solution of potassium hydroxide. The precipitate thus obtained is filtered, washed, dissolved in nitric acid, and evaporated to crystallisation. If the aqueous solution is slowly evaporated, granular masses of the nitrate are obtained, but if crystals are required, the solution must be evaporated nearly to crystallisation, rapidly cooled, after having

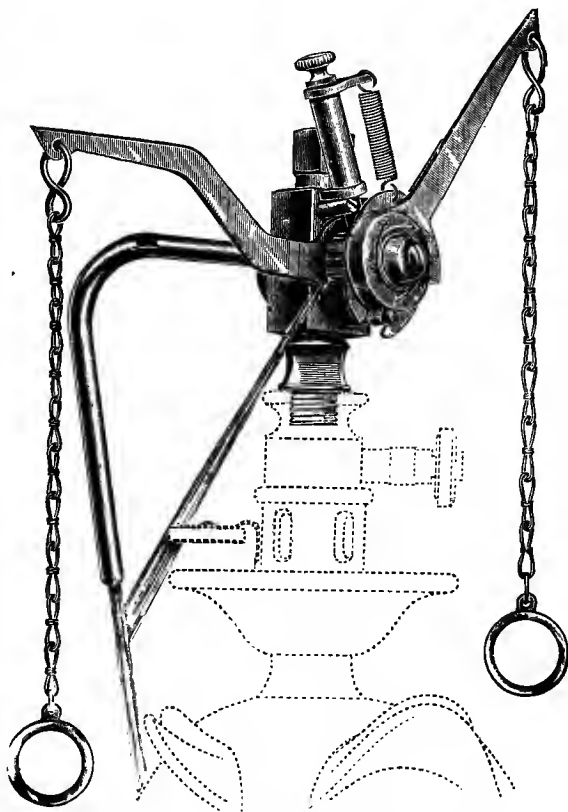


FIG. 23.—Automatic Lighter for Inverted Burners.

added a crystal of the nitrate. The salt, being deliquescent, must be rapidly drained, and dried by pressure.

### Minor Uses for the Cerium Earths and their Salts

Numerous attempts have been made to utilise the reducing power of cerous compounds in the **textile industry**, a recent example of which is the following:—

The yarn is treated with a solution of cerous chloride (sp. gr. 1.16 to 1.26), dried and passed through a bath of strongly alkaline sodium hypochlorite. After being again dried, it is woven with untreated yarn, and when the fabric thus produced is treated with a direct cotton dye and then run through an acid bath, the treated fibres lose their colour, and so a variegated pattern is produced (German Patent, 241,469, 1911). When “vat” or “thio” colours are used the reverse change takes place.

The cerium earth oxides have recently been suggested for use, with tin compounds, for weighting silk (E. Stern, *Zeits. angew. Chem.*, 1914, **27**, 357).

**In leather dyeing**, salts of the cerium earths have been employed as mordants (see F. Garelli, *Collegium*, 1912, 418, and W. Eitner, *Gerber*, 1911, **37**, 199 and 213).

As a **base for dye stuffs** of the alizarin group, certain cerium salts are stated to be very suitable (see O. N. Witt, *Chemische Ind.*, 1896, **19**, 156; also C. Baskerville and T. B. Foust, *Journ. Soc. Chem. Ind.*, 1904, **23**, 104).

**In glass manufacture** several of the cerium earths have been employed as colouring agents. Thus, if 1 per cent. of cerium oxide be added to potash glass, a clear yellow colour results, which is intensified as the quantity is increased, and finally becomes brown. **Neodymium** and **praseodymium**, the two oxides which constitute the mixture often termed didymium, are sometimes used in the manufacture of blue optical glass (see O. Schott, *Jahres. über Fortschr.*, 1889, **42**, 2,685, and German Patent, 103,441).

**Porcelain** is sometimes coloured by the addition of phosphates of **neodymium** and **praseodymium**; the former giving an amethyst-red colour, whilst the latter produces a bright green (see W. Muthmann, Weiss, and H. Heramhof, *Annalen*, 1907, **355**, 144).

The separation of the oxides of neodymium and praseodymium from the other cerium earth oxides found in monazite is a somewhat lengthy process, and the products obtained are not of sufficient technical importance to justify a full description here. Two general methods may be employed—(1) Fractional precipitation utilising the difference, in basiscity of the metals (see W. Muthmann and H. Rolig, *Ber.*, 1898, **31**, 1718; R. J. Meyer and E. Marckwald, *Ber.*, 1900, **33**, 3009; G. P. Drossbach, *Ber.*, 1902, **35**, 2826; Urbain, *Ann. Chim. Phys.*, 1900, **19**, 184). (2) By means of fractional crystallisation (see Dennis and Chamot, *Journ. Amer. Chem. Soc.*, 1897, **19**, 779; C. Scheele, *Ber.*, 1899, **32**, 409; Demarcay, *Comptes rend.*, 1900, **130**, 1019 and 1185; R. J. Meyer, *Zeits. anorg. Chem.*, 1904, **41**, 94; Muthmann and Weiss, *Annalen*, 1904, **331**, 1).

The cerium earths have been found suitable for use as **catalysts** in many chemical operations. Thus, in the formation of sulphuric acid from sulphur dioxide and oxygen, crude cerium earth sulphates may be employed (German Patents, 142,144 and 149,677).

The use of the chlorides of the cerium earths for the production of chlorine from a mixture of hydrochloric acid and air has been patented (German Patent, 150,226). The gaseous mixture is passed over the chlorides, which are heated to a temperature of 350° to 480° C.

**In photography**, ceric sulphate has been suggested for use in reducing the density of negatives (German Patent, 123,017). It has also been found that paper soaked in cerium sulphate, or nitrate, is sensitive to light, and the image produced can be developed by means of phenol or amido-benzoic acid (see A. and L. Lumière, *Comptes rend.*, 1893, **116**, 574).

**In medicine**, the mixed cerium earth oxalates have been used to minimise



nausea, and didymium salicylate has been sold under the name of "Dymal" as a non-irritant antiseptic dressing for wounds.

Cerium sulphate has been patented as a constituent of an **electric accumulator** (English Patent, 21,566, 1900; see also *Zeits. Elektrochem.*, 1902, 298). It was found by W. Krilitschewsky ("Zur Kenntniss des Cersulphat Akkumulators," Halle a/S., 1904) that cerium sulphate accumulators had certain advantages over those made of lead.

For a full account of the various uses to which the cerium earths may be put, see C. R. Böhm, "Die Verwendung der Seltenen Erden," Leipzig, 1913.

### Estimation of Cerium in Minerals and Alloys

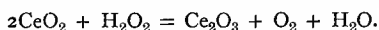
In view of the increasing use of cerium compounds in chemical technology, methods for the estimation of this constituent may be here briefly quoted, but it is impossible, in the space available, to give an adequate account of all the processes which have been employed.

The mineral is first attacked either by heating it with sulphuric acid or by fusion with potassium bisulphate. After treating with water, filtering, and well washing the insoluble matter, the thorium and cerium earths are precipitated as oxalates (see p. 10). The oxalates are filtered off, washed, transferred to a beaker, and boiled with fuming nitric acid until completely decomposed, and the cerium in this solution is separated by conversion to the hydrated ceric oxide. This can be accomplished by several processes, some of which are outlined below.

**Chlorine Process.**—This method, originally introduced by Mosander (*Journ. prakt. Chem.*, 1843, 30, 276), consists in suspending the rare earth hydroxides in a 5 per cent. solution of potassium hydroxide, and passing a current of chlorine through the solution until it is no longer alkaline, and the precipitate has attained a bright yellow colour. This treatment causes the cerium to be precipitated as the insoluble ceric hydroxide, whilst the remaining rare earths pass into solution as chlorides and hypochlorites. After being allowed to stand for a few hours the solution is filtered, the precipitate well washed, dissolved in hydrochloric acid, and the above treatment repeated. The ceric hydroxide is finally dissolved in hydrochloric acid, precipitated as oxalate, and weighed, after ignition, as the dioxide  $\text{CeO}_2$ . A modification of the above process, introduced by E. Browning and E. J. Roberts (*Amer. Journ. Sci.*, 1910, 29, 45), consists in using bromine in place of chlorine.

**Permanganate Process.**—The oxidation of the cerous compounds can also be carried out by means of potassium permanganate. The solution of the rare earths, which must contain only nitrates, is made nearly neutral with sodium carbonate, heated to boiling, and then a dilute solution of potassium permanganate is run in slowly until the pink colour begins to become permanent. A mixture containing potassium permanganate and sodium carbonate, in the ratio of 1 molecule to 4 molecules, is run into the boiling solution until an excess of potassium permanganate is present. When the reaction is complete the precipitated hydroxides of cerium and manganese are filtered, washed, dissolved in hydrochloric acid, and the treatment repeated. The precipitate finally obtained is dissolved in hydrochloric acid, and the cerium separated from the manganese by precipitation as the oxalate, which, after ignition, is weighed as the dioxide  $\text{CeO}_2$ . A full account of this method is given by E. J. Roberts (*Amer. Journ. Sci.*, 1911, 31, 350).

**A Volumetric Process** for the estimation of cerium in the presence of lanthanum and didymium has been introduced by G. von Knorre (*Zeits. angew. Chem.*, 1897, 10, 685, and *Ber.*, 1900, 33, 1924). The process is based upon the fact that ceric salts are reduced to cerous by hydrogen peroxide, and that ammonium persulphate in sulphuric acid solution converts cerous salts to ceric. To the solution of cerous salts in dilute sulphuric acid 2 gm. of ammonium persulphate is added, the solution heated to boiling, cooled to 50° C., a further quantity of 0.5 gm. of persulphate added, the solution boiled for five minutes, cooled, another 0.5 gm. of persulphate added, and the solution finally boiled for fifteen minutes with the addition of a further quantity of sulphuric acid in order to decompose the remaining persulphate. After cooling the solution, excess of a standard solution of hydrogen peroxide is added, and the amount not utilised in reducing the ceric sulphate is estimated by titration with a standard solution of potassium permanganate. The reduction of the ceric salt may be expressed as follows:—



For details of the precautions which are necessary in the carrying out of this determination the original papers should be consulted.

A process for the analysis of pyrophoric alloys has been described by H. Arnold (*Analyst*, 1914, 39, 415).

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## CHAPTER II



## Titanium



## CHAPTER II

# TITANIUM

### LITERATURE

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TITANIUM is often described as being one of the rarer metals, but this is hardly correct, as it constitutes one of the ten most common metals found in a state of combination on the earth's surface. Its oxide is a constituent of many soils and plant ashes.

### Natural Occurrence

The most common mode of occurrence of this element in nature is as the dioxide ( $\text{TiO}_2$ ), either alone as the mineral rutile, or in combination with ferrous oxide as the mineral ilmenite.

**Rutile** usually occurs as a black or reddish-brown mineral having a specific gravity of about 4.3, and containing 98 to 99 per cent. of titanic oxide ( $\text{TiO}_2$ ), together with 1 to 2 per cent. of ferric oxide ( $\text{Fe}_2\text{O}_3$ ).

**Ilmenite**, or titaniferous iron ore, is an iron-black mineral having a specific gravity of about 4.5 and containing a maximum of 52.7 per cent. of titanic oxide ( $\text{TiO}_2$ ), and 47.3 per cent. of ferrous oxide ( $\text{FeO}$ ), corresponding to a formula  $\text{FeO}$ ,  $\text{TiO}_2$ .

Other minerals containing a large percentage of titanic oxide are **sphene** or **titanite** (silicate of calcium and titanium), and **brookite** ( $\text{TiO}_2$ ).

Another mineral called **strüverite**, containing a large but variable percentage of titanium, has been found recently in South Dakota, U.S.A., Federated Malay States, Madagascar, and also in Piedmont, Italy. A paper by T. Crook and the author describing this mineral, as found in the Federated Malay States, and its chemical analysis, will be found in the *Min. Mag.*, 1912, 16, 224.

Analyses of typical specimens of certain of these minerals are given in the following table :—

TABLE X.

	Formula.	1.	2.	3.	4.	5.
		Picro-ilmenite. Ceylon.	Ilmenite. Carolina. Ilmen Mts.		Sphene. Georgetown, D.C.	Strüverite. Fed. Malay States.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Titanium dioxide	TiO <sub>2</sub>	64.72	52.73	45.93	40.82	45.74
Ferrous oxide	FeO	16.59	33.08	36.52	...	8.27
Ferric oxide	Fe <sub>2</sub> O <sub>3</sub>	2.66	8.08	14.30	...	...
Lime	CaO	...	...	...	28.08	...
Magnesia	MgO	15.76	5.33	0.59	0.40	...
Silica	SiO <sub>2</sub>	0.70	...	...	30.10	0.20
Manganous oxide	MnO	0.42	...	2.72	...	trace
Niobic oxide	Nb <sub>2</sub> O <sub>5</sub>	...	...	...	...	6.90
Tantallic oxide	Ta <sub>2</sub> O <sub>5</sub>	...	...	...	...	35.96
Stannic oxide	SnO <sub>2</sub>	...	...	...	...	2.67
Water	...	...	...	...	0.54	0.50

1. "Report on Mineral Survey of Ceylon," Col. Rep. Misc. Ser., Cd. 3762.

2, 3, 4. Dana's "Mineralogy," 6th Edition, pp. 218 and 712.

5. S. J. Johnstone, *Min. Mag.*, 1912, 16, 224.

Of the minerals described above the most common form is **rutile**, but large deposits are rarely found. On the other hand the less pure **ilmenite** is known to occur in large quantities in many localities. Titanic oxide is also a minor constituent of many iron ores and bauxites.

### Geographical Distribution of Titanium Ores

In view of the somewhat limited demand at the present time for titanium minerals, it will suffice to mention only those deposits which have been already worked to some extent.

In **Europe**, the deposits of rutile near Kragero, situated to the north-east of Kristiansund, in Norway, yield about 50 tons per annum of high grade rutile concentrates.

In the **United States**, rutile deposits have been worked for some years at Roseland, near Arrington, Nelson County. The mineral here constitutes about 4 per cent. of certain pegmatite dykes, and by crushing and concentration a product containing over 98 per cent. of rutile is obtained (*Mineral Resources of United States*, 1908, pt. 1., p. 744).

In the **Australian Commonwealth**, small quantities of rutile have been produced from Talunga, South Australia (*Records of Mines, S. Australia*, 1908, 356).

**Commercial Value of Titanium Minerals.**—As with many of the less commonly used minerals, this is largely a matter of negotiation between buyer and seller.

In Great Britain there is very little demand for titanium minerals, even of the highest grade. In the United States titaniferous iron ore from the Adirondack Mountains, which has 14 to 45 per cent. TiO<sub>2</sub>, is reported to be sold for the manufacture of ferro-titanium at £1 to £2 per ton (nominal) according to the titanium content.

The sale of rutile concentrates appears to be on a somewhat more definite basis, but the demand is small. According to one of the largest producers, they are selling three grades of ore :— A grade, containing 95 per cent. of titanium dioxide (TiO<sub>2</sub>), and only traces of iron, at \$160 per ton (2,000 lbs.); B grade, which contains 75 to 80 per cent. of TiO<sub>2</sub>, and the remainder chiefly iron,

sells at \$80 per ton; C grade, which is largely ilmenite, and contains 55 to 60 per cent. of  $\text{TiO}_2$ , sells at \$40 per ton.

**Statistics of Production.**—Complete returns are not available for the production of titanium ore, but the following figures may be of service :—

TABLE XI.

	1910.		1911.		1912.		1913.	
	Tons.	Value.	Tons.	Value.	Tons.	Value.	Tons.	Value.
Norway*	50	£ ...	76	£ 1,300	100	£ 1,900	...	£ ...
United States	505	9,266	Nil	...	6,900	...	7,600	...

### Utilisation of Titanium and its Salts

Up to within a few years ago little use was found for titanium minerals. Numerous attempts had been made from time to time in the United Kingdom and elsewhere to smelt titaniferous iron ore on a commercial scale, but the majority of these were soon abandoned, and at the present time it is difficult to negotiate a sale in the United Kingdom of iron ore containing over 2 per cent. of titanic oxide.

The objections urged against the use of titaniferous iron ore is not that the iron obtained by smelting is of inferior quality, but that under the ordinary working conditions of the blast furnace a pasty slag is produced, and aggregations of titanium nitride and cyanide collect in the higher portions of the furnace. It has been shown, however, that under suitable working conditions the smelting of these ores is commercially possible. This is demonstrated by the fact that iron ores carrying from 8 to 15 per cent. of titanic oxide were smelted successfully for a period of twenty years in the Adirondack Mountains, New York State. Exhaustive articles dealing with the smelting of titaniferous iron ores are given by W. M. Bowron, *Trans. Amer. Inst. Min. Eng.*, 1882, 11, 159; A. J. Rossi, *idem.*, 1893, 21, 832; E. von Maltitz, *Stahl und Eisen*, 1909, 29, 1593, and *Bull.* 64, *U.S. Bur Mines*.

**Ferro Alloys.**—One of the most important uses of titanium minerals at the present time is for the production of ferro-alloys, which are used in the final purification of steel and cast iron.

Many processes for the production of ferro-titanium have been suggested and tried on a small scale; references to these will be found in the bibliography given at the conclusion of the article by B. Stoughton, quoted above.

For the industrial production of ferro titanium two general processes are in use, one or other of these being employed according to the nature of the alloy desired. For the production of alloys in which the presence of carbon is not objectionable, the process of Rossi can be employed (see U.S. Patents, 609,466-7, 1898; 648,439, 1900; 668,266, 1901; 721,467, 1903; 802,941, 1905; 822,305, 1906; 877,518, 1908; 935,863, 979,393-4, 986,505, 992,422-3, 1911; 1,003,805-7, 1,019,526-31, 1,020,512-7, 1,022,595-600, 1,022,799, 1,023,331-4, 1,024,476, 1,025,426, 1,028,389, 1,029,637, 1,032,432, 1,039,672).

In this process the finely pulverised titaniferous iron ore is mixed with charcoal and heated in an electric arc furnace of the Siemens type to a temperature of not less than  $1,927^{\circ}\text{C}$ . ( $3,500^{\circ}\text{F}$ ). This yields an alloy containing 15 to 18 per cent. titanium, 5 to 8 per cent. carbon, and the balance iron.

The second type of process is employed if an alloy free from carbon is desired, the reduction being performed by some substance other than carbon, and for this purpose aluminium is frequently used.

A quantity of scrap aluminium is melted in an electric furnace, into which is charged the requisite quantity of scrap iron or high grade iron ore, the latter

\* Chiefly rutile.

being employed if an alloy quite free from carbon is required. In either case a layer of molten iron forms at the bottom of the bath, and on this the aluminium floats. Upon this layer is charged rich titaniferous iron ore, which is immediately reduced to the metallic state, and combines with the iron already in the bath. So much energy is evolved during this reaction that little current has to be supplied in order to maintain the bath at reaction temperature. The process is capable of yielding alloys containing up to 75 per cent. of titanium, with only 0.12 to 0.80 per cent. of carbon. A full description of the process is given in *Electrochemical Industry* (New York), 1903, I, 527.

According to a recent patent of A. J. Rossi (U.S. Patent, 1,039,672, 1912), **carbide of titanium** is quite as efficient as a steel purifier if intimate mixture with the molten metal is effected.

It is claimed that the alloy is cheaper to produce than ordinary ferro-titanium. The composition of such an alloy is shown in column 5 of the following table :—

TABLE XII.

	Formula.	Ferro-Titanium.					
		1.	2.	3.	4.	5.	6.
		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Titanium -	Ti	10.28	25.17	35.64	17.79	22.21	23 to 25
Carbon	C	0.28	0.59	0.75	7.46	0.80	<i>Nil</i>
Phosphorus	P	0.09	0.06	0.06	0.05	trace	0.05
Sulphur	S	0.01	0.01	...	0.08	trace	0.01
Aluminium	Al	...	...	...	0.80	7.27	5.0
Silicon	Si	...	...	...	1.41	0.92	1.0

1, 2, 3. A. J. Rossi, *Mineral Industry*, 1900, 9, 720.

4. Product of Titanium Alloy Manufacturing Co., made under U.S. Patent, 1,039,672, 1912.

5. Product of Titanium Alloy Manufacturing Co., made under U.S. Patent, 648,439, 1900.

6. Made by Goldschmidt process.

Another form in which titanium is employed to a limited extent in the steel industry is that of titanium "Thermit." This consists of an intimate mixture of titanous oxide and metallic aluminium, which, when added to the molten steel, reacts to give metallic titanium.

**Ferro-titanium** has been largely used in the United States, particularly during the last few years, in the final treatment of steel. Its efficiency as a purifying agent is stated to be due largely to the great affinity which titanium has for nitrogen and oxygen at temperatures above 800° C. Nitrogen in steel, according to the observations of various workers, tends to cause brittleness and segregation of sulphur and phosphorus in the finished product. The titanium is not added to the steel in order to give the latter new properties, as are many other metals, such as tungsten, molybdenum, nickel, tantalum, chromium, etc., but only as a cleanser, and in the finished steel practically no titanium remains. The alloy which finds most frequent use for this purpose is one containing from 15 to 18 per cent. of titanium; alloys containing much larger percentages of titanium are difficult to use owing to their high melting point. The amount of the alloy to be added to each ton of steel as it runs into the ladle after recarburisation varies largely with the nature of the final product. When treating low carbon steels, such as those used for wire or plate, from 2 to 4 lbs. of ferro-carbon titanium is used per ton of steel, whilst for rail steel about 15 or 20 lbs. is used. From 4 to 8 lbs. of the alloy is added to each ton of steel castings, whilst 8 to 10 lbs. is used for axle steels.

This treatment has been applied with considerable advantage to Bessemer, open hearth, crucible, and even electric steel. It has also been applied with equally satisfactory results to cast iron.

The gradually widening use of these alloys in steel manufacture is demonstrated by the fact that in 1912, in the United States of America alone, over 550,000 tons



of titanium-treated steel was produced, whereas the quantity so treated in 1910 and 1911 was 326,300 and 410,600 tons respectively. These quantities are exclusive of cast iron so treated.

Articles dealing with the properties and advantages claimed for titanium-treated steel will be found in articles by R. Moldenke, *Trans. Amer. Foundrymen's Assoc.*, 1908, **17**, 57; W. Venator, *Stahl und Eisen*, 1910, **30**, 650; *Journ. Indust. and Eng. Chem.*, 1910, **2**, 299.

Alloys of titanium with the non-ferrous metals have been employed in small quantity in the past.

An alloy of **copper and titanium** containing 5 to 12 per cent. of the latter constituent has been used for improving copper castings. The addition of 1 to 2 per cent. of this alloy to the molten copper is said to be of great advantage, as the metal can then be cast in sand without difficulty. The alloy also eliminates oxides and absorbed gases, and gives the casting a close dense structure free from blowholes. The influence of titanium on copper and its alloys is discussed by F. O. Bense ( *Metal und Erz*, 1914, **11**, 10 and 46). The addition of **titanium to aluminium** to the extent of about 2 per cent. is said to greatly increase the toughness and resiliency of the metal, but the product is stated to be of somewhat doubtful durability.

**Silico-titanium** is prepared for use in the steel industry, when it is desirable to add silicon as well as titanium, by smelting a mixture of rutile, carbon, and silver sand in an electric arc furnace (*Journ. Soc. Chem. Ind.*, 1910, **29**, 636; French Patent, 407,858, 13th October 1909).

Alloys can be made in this way containing 20 to 75 per cent. of silicon and 5 to 70 per cent. iron (see also United States Patent, 1,019,526).

**Metallic titanium**, other than in the form of its ferro-alloys, has, so far, been put to but few uses. The metal, which has a specific gravity of about 4.8 and a silver-white colour, is hard and brittle when cold, but can be readily forged when red hot. Its observed melting point varies with different experimenters, but is probably between  $1,795^{\circ}$  and  $1,810^{\circ}$  C. When heated to  $600^{\circ}$  C. in oxygen it readily burns to the oxide  $\text{TiO}_2$ , as it also does in nitrogen at  $800^{\circ}$  C., yielding in the latter case several nitrides having the formulæ  $\text{Ti}_3\text{N}$ ,  $\text{TiN}$ ,  $\text{Ti}_2\text{N}_2$ , etc.

This property has been suggested as a means of **fixation of atmospheric nitrogen**, as the nitrides are stated to yield ammonia on treatment with steam or acids (French Patent, 387,002, 1908; English Patent, 1,842, 1908; United States Patents, 957,842-3).

Titanium has also been suggested as a constituent for non-cerium metal **pyrophoric alloys**. A suitable mixture, according to French Patent, 419,388, 1910, contains over 10 per cent. of both manganese and antimony, chromium not exceeding 20 per cent., and titanium not exceeding 15 per cent.

In the textile industry **titanous chloride**,  $\text{TiCl}_3$ , and **titanous sulphate**,  $\text{Ti}_2(\text{SO}_4)_3$ , are gradually finding an extensive use owing to their great power as acid reducing agents.

**Titanous chloride** can be prepared by various processes, amongst which may be mentioned that of H. Spence (French Patent, 324,835, 1902), which consists in electrolytically reducing a hydrochloric acid solution of titanium hydrate in the cathode compartment of a divided cell. The anode employed consists of carbon plates in dilute hydrochloric acid and the cathode of lead plates.

In the dyeing of cotton goods with direct colours it sometimes happens that too deep a shade is obtained, or the colour is uneven, and it then becomes necessary to remove ("strip") it and redye the goods. This "stripping" can be performed, in a few minutes, by immersing the fabric in a solution containing an amount of titanous sulphate varying from 1 to 5 per cent. of the weight of material to be treated.

Certain dyes, such as primuline yellow, thioflavine S., cannot be stripped by this means, whilst the action is rather slow in the case of paranitraniline red and naphthylamine claret.

Titanous chloride and sulphate, which often come on to the market in the form of 20 per cent. solutions, are also used for clearing the whites of coloured goods when the colour has a tendency to "bleed" into the white. They find a similar use in laundry work for clearing articles that have "run" during washing, and are also employed to remove iron mould stains.

**Potassium titanium oxalate** is now used for the mordanting and dyeing of leather. Titanium salts unite with the tannin matter of leather to give a yellow

to brown titanium tannate, which is fast to light and soap (see J. Hurst, *Journ. Soc. Dyers*, 1903, **19**, 105).

Basic **sodium-titanium sulphate** has been patented by M. C. Lamb for use in tanning (French Patent, 327,945 of 1902).

**Titanium lactates** have recently been employed as mordants and "strikers" in the leather industry under the name of "**Corichrome**."

A recent account of the uses to which the compounds have been put is given in *Leather Trades Review*, 1913, **46**, 183 and 266. The use and manufacture of these compounds is covered by English Patents, 22,629, 1901; 23,188, 1901; 14,921, 1902; 27,597, 1902; German Patents, 126,598, 1900; 136,009, 149,577; French Patent, 327,528, 1902. The solutions are prepared, according to English Patent, 22,629, 1901, by acting on freshly precipitated titanium hydroxide with lactic acid and an alkali, or if an excess of lactic acid is undesirable, the solution of titanium hydroxide in hydrochloric, sulphuric, or oxalic acid is acted upon by a lactate of a base which does not form an insoluble salt with the acid in which the titanium hydroxide is dissolved.

Various titanium salts have been employed as mordants for animal fibre (wool, etc.). Amongst these may be mentioned a solution of titanium tetrachloride ( $\text{TiCl}_4$ ) and cream of tartar.

A discussion of the advantages of titanium salts as mordants and their preparation will be found in papers by J. Barnes, *Journ. Soc. Chem. Ind.*, 1896, **15**, 420; 1899, **18**, 15. Their use for fixing colours on vegetable fibre is described in English Patent, 8,589, 1898.

General articles dealing with the use of titanium salts in dyeing will be found:—F. Erban, *Chem. Zeit.*, 1906, **30**, 145; C. Dreher, *Textile Colourist*, 1903, **25**, 4.

**Pigments.**—Titanium compounds have been employed for this purpose to a limited extent. A method of producing pigments from titaniferous iron ore has been patented (French Patent, 412,563, 12th February 1910). The process consists in roasting titaniferous iron ore so as to obtain a uniform product free from concretions, and then crushing in water. The colour of the pigment can be made to vary from yellow to red according to the conditions of roasting.

The light yellow pigments, stated to be suitable for use in rust-preventing paints, can be made by heating titaniferous iron ore with sulphuric acid and subsequently heating the mass to a temperature sufficient to decompose the sulphates (English Patent, 10,368, 1911).

Finely ground rutile is sometimes employed in the ceramic industry to give a soft yellow under-glaze colour to porcelain ware. Titanic oxide is also employed for tinting artificial teeth. Recently, the addition of titanic oxide in quantity varying from 0.1 to 2.0 per cent. has been found to improve fused quartz ware, which is sold under the name of "T. siloxied."

**Illuminants.**—Titanium carbide produced in the electric furnace is employed, to a small extent, in the United States, for the manufacture of electrodes for arc lamp lighting. These are produced by mixing the finely ground carbide with a suitable binder, and shaping the paste by hydraulic pressure. The rods so produced, after drying in a gas oven, are heated in a carbon tube electric furnace. The electrodes are next partly coated with copper to prevent oxidation during burning. The use of titanium carbide as electrodes has not found very extensive application, probably because the light is of a somewhat yellow character, and the operating costs are rather high (see also German Patent, 231,231, 1910). Another form of flame arc electrode consists chiefly of carbon, together with calcium titanate, an organic salt of titanium and a titanium halogen compound or alkali titanofluoride (U.S. Patent, 1,112,458, 1914). See also cerium titanofluoride, p. 30.

According to English Patent, 18,220 of 1912, a luminous arc electrode can be made from a mixture consisting of 96 per cent. of titanium carbide, 3 per cent. of copper oxide, and 1 per cent. of lithium fluoride. The latter substance is stated to steady the flame without imparting any undesirable colour. Titanic oxide, together with calcium cyanamide, cryolite, and carbon, is a mixture suggested for electrodes in English Patent, 11,792 of 1912 (see also English Patents, 2,027, 18,965, 1909; 17,278, 1910; 710, 17,723, 1911; 6,500, 1912).

**Titanium carbide** was used for the production of incandescent electric lamp filaments for a short time, but is now displaced by the more economical metallic filaments, tantalum and tungsten, *q.v.* Its initial efficiency was about 2.5 watts per candle power (English Patent, 14,852, 1908).

The "magnetite" arc lamp has its positive electrode composed of a mixture of magnetite and chromite, together with 15 to 25 per cent. of rutile, or an equivalent amount of ilmenite. This lamp can be operated only on a direct current circuit, as the magnetite must act as the positive electrode. This lamp, which has found favour in certain districts in the United States, and is now being used in this country, is said to give a very uniform distribution of light in the horizontal plane. For this use the minerals must be very finely ground, and to attain this end they are first crushed between rolls, and the final grinding is done in a ball mill.

### Analysis of Titanium Minerals and Salts

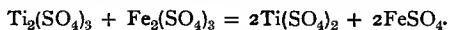
It is not possible in the space available to give an adequate account of the methods of analysis, but the following brief outline may prove of service.

The mode of estimating the quantity of titanium in a mineral varies largely with the amount and the nature of the other constituents present. Thus, the presence of tantalum, niobium, uranium, vanadium, or zirconium renders the gravimetric estimation of titanium a matter of considerable difficulty. A method suitable for the estimation of titanium in the presence of the first two elements has been described by the author in the *Min. Mag.*, 1912, 16, 224.

In the absence of vanadium and large quantities of iron, titanium can be estimated colourimetrically by the following process:—About 0.5 to 1.0 gm. of the finely ground mineral is fused, at a low temperature, for about half an hour, with ten times its weight of potassium bisulphate. After being allowed to cool, the melt is crushed and extracted with about 200 c.c. of cold 5 per cent. sulphuric acid, to which has been added 10 c.c. of "10 volume" strength hydrogen peroxide. When the extraction is complete, the solution is filtered, the filtrate made up to 500 c.c., and the titanium in it estimated by the A. Weller colourimetric method (*Ber.* 1882, 15, 2, 593). This consists in matching the colour of the solution against that produced when hydrogen peroxide is added to a standard solution of a titanium salt. The accuracy of the estimation is seriously affected by the presence of fluorides, and to a less degree by potassium sulphate and iron salts. A full account of this method is given by W. F. Hillebrand in "The Analysis of Carbonate and Silicate Rocks," *Bull.* 422, *United States Geol. Sur.*, pp. 128-34.

This method is accurate for minerals containing up to 10 per cent. of titanic oxide, but if used for estimating larger amounts it is not reliable, owing to the difficulty of matching the colours produced by strong solutions, or the error introduced by the large dilutions necessary if weak solutions are employed.

In the absence of compounds such as salts of niobium, vanadium, or uranium, which, in the reduced state, are oxidised by ferric salts, titanium can be estimated by reducing it to the titanous condition by means of zinc in acid solution, and then titrating with a solution of ferric alum, in an inert atmosphere, using ammonium thiocyanate as indicator. The reaction proceeds in accordance with the equation—



This method is of value, as it permits of the rapid and accurate estimation of titanium in the presence of iron compounds. The reduced solution can also be titrated with a standard solution of potassium permanganate, but, in this case, allowance must be made for any iron present.

For a full account of the processes available for the estimation of titanium and its separation from other elements see "Die Analyse der Seltenen Erden und der Erdsäuren," by R. J. Meyer and O. Hauser (Stuttgart, 1912). Methods of analysis of ferro-titanium are given in "The Chemical Analysis of Special Steels," by C. M. Johnson (London, 1909).

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## CHAPTER III



### *Zirconium*



## CHAPTER III ZIRCONIUM

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ZIRCONIUM belongs to the same group in the periodic system as thorium, cerium, and titanium, but, at the present time, its commercial utility in nowise approaches that of any of these.

The oxide, zirconia, was first isolated in 1789 by Klaproth, from Ceylon zircon, but the metal was not produced until 1824, when Berzelius obtained it by reducing the double fluoride of potassium and zirconium with metallic potassium.

### Natural Occurrence

Zirconium does not occur in the metallic form in nature, but the ortho-silicate, **zircon**, is of fairly common occurrence in certain localities, and large deposits of the oxide, **baddeleyite**, have been located in Brazil.

**Zircon** is a silicate of zirconium, and, when pure, contains 66.2 per cent. of zirconia ( $ZrO_2$ ) and 33.8 per cent. of silica; impure forms also contain small quantities of iron oxide and combined water. It is found as a brown opaque mineral having a conchoidal fracture and an adamantine lustre. Zircon is sometimes found in clear forms which may be colourless, yellow, or red, and these are used as gemstones under the name of *hyacinth* (see p. 50). The specific gravity of ordinary zircon is about 4.7.

**Baddeleyite** was formerly a mineral of somewhat rare occurrence, but, during the last few years, fairly large quantities have been found in the gravels of the Sierra de Caldas of Minas Geraes. According to E. Wedekind, the mineral is available in three forms—(1) black glassy pieces; (2) broken stony fragments; (3) pebbles. Analyses of these three varieties are given in Table XIII. The commercial product is a mixture of all three forms, and has the composition shown in column 6. By crushing and sieving, the glassy variety can be freed from much of its iron oxide, which occurs in cavities in the mineral.

The percentage composition of the more important zirconium minerals is given in the following table:—

TABLE XIII.

	Zircon.		Baddeleyite.				
	1. Ceylon.	2. Norway.	3. Brazil. Glassy Variety.	4. Brazil. Stony Variety.	5. Brazil. Pebbles.	6 Brazil. Commercial Variety.	7. Ceylon.
	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Zirconia, $ZrO_2$	66.35	64.05	94.12	88.40	74.48	68.93	98.90
Ferric oxide, $Fe_2O_3$	0.83	2.85	3.22	4.07	10.26	3.59	0.82
Titanic oxide, $TiO_2$	...	...	0.98	3.12	1.35	0.60	...
Lime, $CaO$	...	...	...	...	...	...	0.06
Silica, $SiO_2$	32.35	32.53	2.41	5.89	14.08	26.30	0.19
Water, $H_2O$	0.23	...	...	...	...	0.80	0.28

1. "Rep. Mineral Survey Ceylon," Col. Rep. Misc. Series, Cd. No. 3,762, p. 60.

2. E. S. Dana, "Descriptive Mineralogy" (London, 1906), p. 485.

3 to 6. E. Wedekind, *Ber.*, 1910, 43, 290.

7. G. S. Blake, *Min. Mag.*, 1907, 14, 383.

**Preparation of the Mineral Before Use.**—The commercial variety of baddeleyite, having the composition shown above, usually contains too much iron and silica to be used without previous treatment. The method of purification suggested by E. Wedekind consists in boiling the pulverised mineral in strong hydrochloric or sulphuric acid, which removes most of the iron and titanic oxides. When necessary, the silica is removed by treating the mineral with hydrofluoric and sulphuric acids, followed by ignition. This treatment is usually sufficient for most technical purposes.

If the pure oxide of zirconium is required, the method of L. Weiss, which is often technically employed, can be used. This process, which is suitable for treating either zircon or baddeleyite, is as follows: 50 kg. of baddeleyite or 70 kg. of zircon is intimately mixed with 150 kg. of sodium carbonate and 250 kg. of borax. The whole mixture is placed in a special cast-iron vessel, and heated in a reverberatory furnace. The melt is stirred frequently until decomposition is complete, and, after cooling, is finely ground and lixiviated with water. The insoluble matter, which contains the iron, titanium, and some sodium zirconate, is removed by filtration, and is reserved for further treatment. The solution, which has a specific gravity of about 1.16, is concentrated by the aid of steam in an iron boiler, until it has a specific gravity of 1.32 to 1.36, when it is allowed to cool and crystallise, with occasional agitation. The crystals obtained are sufficiently pure to be used without further treatment. The mother liquor is used for lixiviating further fusions, and the silica which accumulates is removed from time to time by passing carbon dioxide into the solution.

Another method, devised by R. Bayer (*Zeits. angew. Chem.*, 1910, 23, 485), consists in heating one part of the ground mineral with 2.5 parts of barium carbonate in a graphite crucible, which is placed in a wind furnace and the temperature maintained at about 1,400° C. for two hours. After cooling, the melt, which contains barium zirconate, is extracted with hydrochloric acid and the solution evaporated to dryness to precipitate silica. The residue is taken up in acid and let crystallise until first barium chloride, and later zirconium oxychloride, separate out. This latter substance is dissolved in water and the zirconium precipitated by ammonia.

### Industrial Utilisation of Zirconium and its Salts

Up to within a few years ago, little use was found for zirconium compounds. One reason against the development of their industrial employment was that the only commercial source of fairly pure zirconia was the mineral zircon, and the high cost of preparing the oxide from this material rendered its use impossible.



The already-mentioned discovery of large quantities of zirconium oxide in Brazil gave an impetus to the further investigation of the refractory properties of the material, and the greater proportion of the zirconia now utilised is obtained from this source.

**Refractory Materials.**—Pure fused zirconia ( $\text{ZrO}_2$ ) has a very low coefficient of expansion (linear = .00000084), and is, therefore, of service for the production of vessels of a refractory nature which are to be subjected to large or sudden changes of temperature. Vessels made of this substance can be plunged whilst white hot into cold water without risk of fracture. Owing to the high melting point of zirconia, considerable difficulty is experienced in making it into vessels, and most of the published processes include the use of some binding agent, often an alkali, to assist in fritting the mixture. A process described by L. Weiss (see above) for the manufacture of refractory crucibles consists in the use of a mixture of 90 parts of zirconia, 10 parts of magnesia, together with 10 per cent. of phosphoric acid as a binding agent. The ware, after firing in the electric furnace at a suitable temperature, is stated to be very resistant and practically unaffected either by molten alkali or potassium bisulphate.

Zirconia would appear to be very suitable for use as a furnace lining, owing to its resistance to the corrosive action of steel, copper, red brass, etc. Experiments have shown that the maintenance cost of a Siemens-Martin steel furnace, lined with crude zirconia, was only one half of that entailed when linings of other refractory substances were used. Water-free tar may be used as a binding material.

Another process described by R. Bayer consists in making an intimate mixture of gelatinous zirconium hydroxide and raw zirconia (purified, as previously described, by crushing and treating with hydrochloric acid), together with the addition of a small quantity of starch paste as a binding agent. After being moulded to the desired shape, the crucibles are air-dried for several days, and then, after drying at  $100^\circ \text{C}$ ., they are heated in an electric resistance furnace of the Hempel type to a temperature of  $2,000^\circ$  to  $2,500^\circ \text{C}$ .

**Metallic Zirconium.**—There are several practical difficulties associated with the production of this metal, as it combines readily with oxygen, nitrogen, carbon, silicon, etc., and therefore cannot be produced by reducing the oxide with carbon in the electric furnace, as this reaction yields the carbide. The difficulty in reducing the oxide, and the readily oxidisable nature and high melting point of the finely divided metal, make its production an expensive matter. It has been prepared by reducing potassium zirconium fluoride with metallic sodium in an iron cylinder, using a layer of fused potassium chloride as protective cover.

According to a recent communication by E. Wedekind (*Annalen*, 1913, 395, 149), unsatisfactory results are obtained by reducing the oxide with either metallic aluminium or magnesium, but a good yield of the metal is obtained by heating the oxide with metallic calcium shavings. The operation is carried out in an iron tube at a pressure of 0.1 to 0.5 mm. of mercury. The product of the reaction is treated successively with water, acetic acid, dilute hydrochloric acid, and water until free from calcium, and is then washed with acetone and dried *in vacuo* at  $300^\circ \text{C}$ . All these operations must be carried out in the absence of air.

Pure zirconium melts at about  $1,300^\circ \text{C}$ ., and has a specific gravity of about 6.4. It is not attacked by sulphuric or nitric acids, but is dissolved in the cold by hydrofluoric acid or aqua regia.

So far, little use has been found for metallic zirconium, but it has been tried as a filament for incandescent electric lamps (*Zeits. angew. Chem.*, 1910, 23, 2065).

**Ferro-Zirconium** is used, to a limited extent, in steel manufacture for removing nitrogen and oxides from the finished product, an alloy containing 20 per cent. of zirconium being added in amount equal to about 1 per cent. of the weight of steel treated (see English Patent, No. 29,376, 1910).

**Zirconia Quartz Ware.**—Recently small quantities of zirconia have been utilised in the manufacture of a variety of quartz ware termed "Siloxide" (French

Patent, No. 432,786, 1911). It is claimed that the addition of a small quantity of zirconia makes the ware more resistant towards the action of metallic oxides, particularly alkalis, and decreases its tendency towards devitrification on heating. The tensile strength is also said to be materially increased.

According to a recent paper by F. Thomas (*Chem. Zeit.*, 1912, 36, 25), the best resistance to devitrification is obtained with ware containing 0.5 per cent. of zirconia, and the best tensile strength with samples containing 1 per cent.

**Zirconium Carbide** has a metallic appearance, and is sufficiently hard to scratch quartz, but not ruby. It has been suggested as an agent for cutting glass and also for abrasive purposes.

It can be produced by heating zirconia with carbon in the electric furnace (H. Moissan and Lengfeld, *Comptes. rend.*, 1896, 122, 651), or by similarly heating zircon with calcium carbonate and carbon, and then extracting the mass with dilute hydrochloric acid. A current of about 600 amperes is stated to be necessary (E. Wedekind, *Ber.*, 1902, 35, 3929; *Chem. Zeit.*, 1907, 36, 654).

**Pigments.**—The use of various zirconium compounds as white pigments has been patented by L. Weiss (German Patent, No. 235,495, 1910). Amongst those compounds mentioned as being suitable are the oxide, silicate, basic carbonate, phosphate, and basic sulphite. All these compounds have a good permanent white colour and covering power, and are non-poisonous. All are unaffected in colour by sulphurated hydrogen, and mix well with the usual paint vehicles.

**Illuminants.**—Zirconia formed an important constituent of the glower of the Nernst lamp (see English Patents, 19,424 and 23,470 of 1897). Rods of zirconia form the incandescent substance of the Blériot lamp (German Patent, 174,313, 1906).

The use of zirconium carbide as a filament for incandescent electric lamps has been patented (German Patent, Nos. 133,701 and 148,257), but has not, so far, proved entirely satisfactory. According to English Patent, 5,412 of 1908, filaments may be made by mixing zirconium oxalate with a binder and sufficient carbon to reduce the oxalate. The use of zirconium nitrate, in place of thorium nitrate, for the manufacture of incandescent gas mantles has been patented, but the invention has not been a commercial success (English Patent, Nos. 1,681 and 4,000 of 1896).

**Other Uses.**—Basic zirconium acetate, or a mixture of soluble zirconium salts with sodium phosphate, has been patented for **weighting silk** (German Patent, No. 232,875). It has also been suggested that zirconia might replace some of the stannic oxide in enamels.

“**Kontrastin**” is the name under which pure zirconia is sold for the purpose of defining the intestines for X-ray photographs.

As **gemstones**, certain clear varieties of zircon have been utilised for many years under the names of **hyacinth**, **jargon**, and **Matura diamond**. The latter is produced by heating a brownish yellow variety of zircon and so causing decolorisation. For further details, see “Precious Stones,” by M. Bauer (London, 1904).

**Commercial Value of Zirconium Ores.**—As there is only a very limited demand for zirconium minerals, there is little possibility of finding a market for any but those of the highest grade, and then only with difficulty. The prices at which the products made from the Brazilian mineral can be purchased are on a fairly definite basis. According to recent information (Jan. 1913), the following grades are offered for sale:—

TABLE XIV.

Grade Mark.	Zirconia. (ZrO <sub>2</sub> .)	Ferric Oxide. (Fe <sub>2</sub> O <sub>3</sub> .)	Silica. (SiO <sub>2</sub> .)	Price per Metric Ton.
	Per Cent.	Per Cent.	Per Cent.	£.
“Crude”	85	...	...	31
“S”	90-92	1	8	35
“N”	90-92	7	1	36
“NS”	98	0.8	1	50

The demand for zircon is much smaller than for the Brazilian baddeleyite, and sales are correspondingly more difficult to negotiate.

**Production.**—Statistics regarding the production of zirconium minerals are somewhat difficult to obtain as the output, from most localities, is very interrupted. In 1911, Brazil produced 25 tons valued at £7,437, and small quantities are occasionally produced from the United States and Norway.

### Estimation of Zirconium in Minerals

Zirconium is usually estimated gravimetrically as the dioxide ( $ZrO_2$ ), which is precipitated from solutions of its salts, in a hydrated form, by excess of ammonia.

Practically all zirconium minerals have to be fused with about five times their weight of potassium bisulphate before they become soluble in acids. After fusion, the melt is leached with a 2 per cent. solution of sulphuric acid, and the insoluble residue separated by filtration, and again fused. The acid filtrates are then treated with sulphuretted hydrogen, any precipitate that may form is filtered off, washed, and the filtrate, after removal of sulphuretted hydrogen, is nearly neutralised with ammonia in the cold, and excess of a saturated solution of sodium thiosulphate added. After standing for a few minutes, the solution is heated to boiling for one hour, let stand for twelve hours, filtered, and the precipitate well washed with boiling water. This precipitate, which contains all the zirconium, tantalum, niobium, thorium, and titanium, also traces of iron and aluminium, is dissolved in hydrochloric acid, and the thorium removed from the solution as oxalate (see p. 10). The oxalate filtrate contains the titanium and zirconium, but in order to recover these the oxalate must be destroyed by evaporating the solution nearly to dryness with concentrated nitric acid. The bases are then precipitated by means of sodium thiosulphate as before. After filtration and washing well with hot water, the precipitate is dissolved in concentrated hydrochloric acid, and after diluting the solution with water, the titanium and zirconium are precipitated together by excess of ammonia. After filtration, and being well washed with water, the precipitate is ignited and weighed as  $ZrO_2 + TiO_2$ . The titanium dioxide in this precipitate can be estimated colourimetrically by the Weller method (see p. 43), and the zirconia obtained by difference.

Methods for the complete analysis of commercial ferro-zirconium have been described by W. Trautmann (*Zeits. angew. Chem.*, 1911, 24, 62), and also by M. Wunder and B. Jeanneret (*Zeits. anal. Chem.*, 1911, 50, 733).



## CHAPTER IV



## Tantalum and Niobium



## CHAPTER IV

# TANTALUM AND NIOBIUM

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TANTALUM is one of those metals whose appearance in commerce, in a pure condition, is of comparatively recent date, and, owing to its peculiar properties, it seems likely that it will find a fairly wide range of utility.

Tantalic oxide ( $Ta_2O_5$ ) was first isolated, in 1802, by Hatchett, from a mineral obtained from Massachusetts, and the metal was produced in an impure form by Berzelius in 1824, by heating potassium fluotantalate with metallic potassium. Although tantalum belongs to the same group of elements as nitrogen, phosphorus, arsenic, antimony, bismuth, and vanadium, in its general properties it appears to have little in common with these elements.

### Natural Occurrence

Tantalum is found in nature only as the oxide ( $Ta_2O_5$ ), and is usually associated with variable percentages of the oxides of niobium, iron, and manganese. It is an essential constituent of about forty minerals, but of these only tantalite is of commercial importance.

**Tantalite** is the most important ore of tantalum, occurring usually as a black mineral having a specific gravity of 6.5 to 7.3, and crystallising in the ortho-rhombic system. When pure, its composition is represented by the formula  $FeO, Ta_2O_5$ , but in most specimens some of the tantalum is replaced by niobium (columbium), and some of the iron by manganese.

**Columbite** is the most commonly occurring mineral containing tantalum. It often occurs associated with tantalite; being essentially a niobate of iron and manganese of the formula  $(Fe, Mn)ONb_2O_5$ , and often crystallises in ortho-rhombic prisms whose specific gravity varies from 5.3 to 6.5. It has been observed that an increase in the percentage of tantalum in the mineral is accompanied by a proportionate increase in its specific gravity, and this relationship has been suggested as a means of roughly estimating the tantalum content of a mineral. Part of the niobium in the mineral is often replaced by tantalum.

Other minerals containing tantalum are **fergusonite** (niobate of yttrium and tantalum), **samaraskite** (niobates and tantalates of iron, calcium, yttrium, and

cerium earths), **yttrio-tantalite** (niobates and tantalates of yttrium, iron, cerium earths, and uranium), **tapiolite** (iron tantalate). At the present time, however, none of these are utilised as commercial sources of tantalum, as the demand for tantalum minerals is small, being more than met by the supply of tantalite, and none but the highest grade of this mineral finds a sale.

### Geographical Distribution of Tantalum Ores

The most important producing localities are the Greenbushes and Pilbara districts of **Western Australia**. The mineral also occurs in certain of the tin bearing districts in the Northern Territory of **South Australia**. In the **United States**, tantalite ores occur, and have been worked near Branchville, Connecticut, and in the Black Hills of Dakota. As a general rule, American tantalite contains from 10 to 40 per cent. of tantallic oxide, whilst the amount of this constituent present in the Australian mineral varies from 50 to 70 per cent.

Tantalum minerals have also been found in certain localities in Finland, Sweden, Norway, Russia, France, Bavaria, Italy, the Federated Malay States, Nigeria, and Ceylon, but at present none of these occurrences are of commercial importance as producers.

The composition of some typical tantalum ores is shown in the following table :—

TABLE XV.

	Formula.	Tantalite.	Columbite, Ceylon.	Samarskite.		Fergusonite.	
		1.	2.	Miask.	India.	Ytterby.	Ceylon.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tantallic oxide	Ta <sub>2</sub> O <sub>5</sub>	76.34	7.30	1.36	13.64	28.50	1.51
Niobic "	Nb <sub>2</sub> O <sub>5</sub>	7.54	67.35	47.47	39.76	29.66	46.06
Ferous "	FeO	...	9.22	...	...	...	0.43
Ferric "	Fe <sub>2</sub> O <sub>3</sub>	13.90	2.05	11.02	12.15	0.76	...
Yttrium earth oxides -	Y <sub>2</sub> O <sub>3</sub> , etc.	...	...	12.61	15.80	33.47	41.22
Cerium "	Ce <sub>2</sub> O <sub>3</sub> , etc.	...	...	3.31	0.67	...	0.82
Uranium oxide -	U <sub>3</sub> O <sub>8</sub>	...	...	11.60	12.09	2.24	3.92
Manganous "	MnO	1.42	10.30	0.96	0.42	...	...
Lime	CaO	...	0.36	0.73	1.07	4.40	...
Magnesia -	MgO	...	...	0.14	0.07	...	...
Thoria -	ThO <sub>2</sub>	...	...	6.05	0.09	...	2.48
Titanium dioxide	TiO <sub>2</sub>	...	2.90	...	1.70	...	0.07
Stannic oxide	SnO <sub>2</sub>	0.70	...	0.50	0.04	...	...
Lead "	PbO	...	...	...	0.68	...	...
Tungstic "	WO <sub>3</sub>	...	...	1.36	...	...	...
Zirconia	ZrO <sub>2</sub>	...	...	4.35	...	...	...
Water	H <sub>2</sub> O	...	...	...	...	...	2.78

1, 3, and 5. *Mineral Industry*, 1908, 17, 800. 2. Col. Rep. Misc. Ser., Cd. 3190, p. 30.  
4. *Bull. Imp. Inst.*, 1913, 10, 483. 6. Col. Rep. Misc. Ser., Cd. 3190, p. 37.

The **production** of tantalum ore is small and variable. During 1909, ore valued at £327 was raised in Australia, but no production was recorded for 1910, 1911, 1912, or 1913.

**Commercial Value of Tantalum Ores.**—The demand for these ores at the present time is very small, and consumers are reported to hold stocks sufficient for several years. The price of tantalum minerals has varied, during the past few years, between £3. 10s. and £1. 10s. per unit of tantallic oxide (Ta<sub>2</sub>O<sub>5</sub>). Buyers often stipulate that ore shall contain over 65 per cent. of tantallic oxide, the niobic oxide must not exceed 3 per cent., and that chromium is to be absent.

**Manufacture of Metallic Tantalum.**—This may be roughly divided into two operations—(1) The separation of the tantalum from the other substances with which it is associated in the ore, and the preparation of a salt of the metal. (2) The electrolysis of a pure salt of tantalum under such conditions as will yield the metal in a fairly pure form.



Tantalum minerals are not readily attacked by the common acids, except perhaps strong hydrofluoric acid, and in order to decompose the mineral it is necessary to heat it for some considerable time with a suitable flux, such as caustic soda or potassium bisulphate. The usual process employed is to fuse the finely ground mineral in an iron crucible, with about three times its weight of potassium bisulphate, and after cooling, to treat the melt with water. By this means most of the oxides, other than those of tantalum, niobium, silicon, and tungsten, pass into solution. The insoluble matter, after being well washed, is digested with ammonium sulphide, so as to remove compounds of tin and tungsten, boiled with dilute hydrochloric acid to remove iron sulphide, and again well washed. The precipitate is next dissolved in hydrofluoric acid and boiled, so as to remove the silica as the volatile silicon tetrafluoride ( $\text{SiF}_4$ ). To the solution is next added an amount of potassium hydrogen fluoride ( $\text{KHF}$ ) slightly greater than is required to form the double salts, potassium fluotantalate ( $\text{K}_2\text{TaF}_7$ ) and potassium fluoxy-niobate ( $2\text{KF}, \text{NbOF}_3 + \text{H}_2\text{O}$ ). The solution is evaporated until, on cooling, it deposits the tantalum salt in the form of rhombic needles which are almost free from the more soluble niobium compound.

This separation, which was first introduced by C. Marignac (*Ann. Chim. Phys.*, 1866, 8, 5), is based upon the fact that, at ordinary temperatures, one part of potassium fluotantalate is soluble in about 150 parts of water, whilst the niobium salt, under similar conditions, is soluble in 12 to 13 parts of water. For a discussion of the properties of potassium fluotantalate, see R. D. Hall (*Journ. Amer. Chem. Soc.*, 1904, 26, 1,235).

The method first used for the production of metallic tantalum is that ascribed to Berzelius and Rose. In this process, as described by W. von Bolton (*Zeits. Elektrochem.*, 1905, II, 45 and 722), potassium fluotantalate is put into a crucible interspersed with layers of metallic sodium, and the reaction started by the application of heat. As soon as the interaction is complete, the mass is cooled and washed first with water, and finally with nitric acid.

The process which has been used recently on a technical scale for obtaining metallic tantalum is that devised by W. von Bolton, and covered by German Patents, 152,848, 152,878, and 155,548 of 1903. The method consists in electrolysing the potassium fluotantalate prepared as described above, and thus obtaining the tantalum in the form of a somewhat impure metallic powder, which is purified by being melted *in vacuo* between tantalum electrodes. By this means the impurities, which are more volatile than the metal, are volatilised.

A process introduced by the British Thomson-Houston Co., somewhat similar to the above, is described in English Patent, 24,234 of 1906. In this method the potassium fluotantalate is electrolysed in a refractory crucible made of magnesia or tantalic oxide, using a cathode of pure tantalum and an anode of impure tantalum.

Another process for purifying the metallic tantalum powder is to compress it into blocks and heat these in a crucible of magnesia or thoria which is lined with metallic tantalum. The heating is conducted *in vacuo* by means of an electric current, using a bar of tantalum as the cathode (English Patent, 21,766 of 1904).

The process devised by G. C. Bouhard (French Patent, 377,931 of 1907) consists in dissolving 100 g. of potassium tantalate in 3 litres of water, and adding sulphuric acid until no further precipitate forms. After being allowed to stand, the solution is filtered, and the precipitate washed and added to 1 litre of water heated from 70° to 80° C. To this solution is added a 20 per cent. solution of oxalic acid in quantity sufficient to dissolve the precipitate, and after neutralising the solution thus obtained with ammonia, sulphuric acid is added in quantity sufficient to make 3 per cent. of the total volume of liquid. The acid solution is now electrolysed between electrodes of carbon or platinum, using a current of 2 volts and 0.1 to 0.3 amperes. When the deposited metal is 3 to 4 mm. thick it is removed from the bath and drawn into filaments.

Pure metallic tantalum cannot be prepared by reducing the oxide with excess of carbon, as, under these conditions, a mixture of carbide and oxide is obtained. A method employed at one

time by W. von Bolton was to mould tantalic oxide with paraffin wax into rods, which, after calcining, were heated *in vacuo* by means of an alternating electric current (*Zeits. angew. Chem.*, 1906, 36, 1,537). The rods of brittle metal thus produced were purified by melting *in vacuo*.

In von Pirani's process the great affinity which metallic tantalum has for hydrogen is utilised as a means of purifying the crude metal. Tantalum will absorb about 740 times its own volume of hydrogen, with the production of a very brittle compound. After saturating the metal with hydrogen it is put into a vessel and made the positive pole of a circuit, whilst the negative pole consists of barytes. The metal is heated to redness, and then an electric current is passed which melts the metal and volatilises the occluded gases and impurities (see also French Patent, 367,293, 1906).

**Properties of Metallic Tantalum.**—In appearance the pure metal much resembles platinum, but its melting point is considerably higher, being, according to recent determinations, about  $2,910^{\circ}$  C. The specific gravity of the pure fused metal is about 16.6, whilst its specific heat is 0.0365. The specific resistance of a bar of the metal 1 m. long and 1 sq. mm. in cross section is 0.146 ohms at  $20^{\circ}$  C. Tantalum is characterised by its great ductility, combined with toughness, and it can be worked by the usual methods employed for other metals.

When first prepared in quantity, the metal was stated to possess unusual hardness (*Zeits. Elektrochem.*, 1905, II, 503), but at a later date this was found to be incorrect, the hardness being due to the presence of small quantities of oxide. When this impurity is removed, the metal is found to be considerably softer and more ductile; the normal hardness of pure tantalum being about equal to that of medium hard steel. Towards chemical action the metal is particularly resistant, being unattacked by solutions of caustic alkali and mixtures of the common acids. It is attacked, however, by hydrofluoric acid, molten alkali nitrates, sulphur, and fused caustic alkali: the latter substance causing the metal to disintegrate into crystals. On heating in air, the surface of the metal turns blue at  $400^{\circ}$  C., greyish black at  $600^{\circ}$  C., and at higher temperatures it becomes coated with a layer of oxide and slowly burns. When heated in hydrogen, it forms brittle compounds of metallic appearance, but when heated *in vacuo* to a white heat by a continuous electric current the metal is little affected.

### Uses of Metallic Tantalum

At the present time, tantalum is perhaps best known as a material used for making the filaments of certain incandescent electric lamps (see p. 78), but there are numerous other uses to which the metal may be put, and a few of these are here described.

**Tools.**—The use of the metal for surfaces and points which will be subject to mechanical wear is covered by French Patent, 351,351 of 1905. Various methods have been introduced for producing tantalum of the requisite hardness for the production of cutting tools, etc. Amongst these is the addition of oxide (English Patent, 6,050 of 1908), treatment with oxygen, hydrogen, silicon, boron, aluminium, titanium, or tin (French Patent, 357,714 of 1905). For the production of hardened tantalum, according to English Patent, 6,051 of 1908, the powdered metal is mixed with 1 to 10 per cent. of silicon, the mixture moulded under pressure, and melted *in vacuo* between tantalum electrodes. From 5 to 10 per cent. of silicon is recommended if the metal is to be used for tools, and 2 to 3 per cent. for wire.

**Dental and Surgical Instruments.**—For these purposes tantalum possesses many advantages, amongst which may be mentioned that it is non-rusting, can be sterilised in acids or in the flame at a moderate red heat, and the instruments can be repeatedly sharpened similarly to those made of steel. For dental purposes, tantalum tools are surface hardened by a secret process, and have a hardness about equal to that of agate (see also *Brit. Med. Journ.*, 1911, 32, 724, and *Dental Review*, 1911, 25, 1,210).

**Chemical Apparatus.**—For many chemical operations, tantalum can be used in place of platinum, and has the advantage of costing considerably less, but it must also be remembered that when no longer fit for use platinum has a market value not far short of that charged for new vessels, whilst it would seem probable that disused tantalum vessels would be of comparatively little value. During 1913, tantalum vessels were sold at 2s. 6d. per gram. There is no evidence that the metal is finding a wide use in the chemical industry.

**Pens.**—The elasticity and hardness which tantalum possesses when rolled into a thin sheet renders it particularly suitable for the manufacture of pens, and it is stated that large quantities are now being made by a firm in Berlin. Pens made of tantalum have the advantage over those made of steel in that they do not rust, and are not corroded by ink. In order to reduce the wear on the point, it is specially hardened, and will then wear at about the same rate as a good quality steel pen.

**Electrodes.**—According to the investigations of O. Brunck (*Chem. Zeit.*, 1913, 36, 1233), tantalum is particularly suitable as an electrode material, as many metals such as silver, copper, zinc, nickel, platinum, and antimony can be deposited on a tantalum cathode, and can be dissolved off by acids or aqua-regia. As tantalum does not form an alloy with zinc at the surface of contact with the liquid, it does not require to be coated with silver or copper before use (see also G. Oosterheld, *Zeits. Elektrochem.*, 1913, 19, 585).

**Alloys.**—Tantalum forms alloys with many metals such as iron, molybdenum, and tungsten, but only the iron alloy is, at present, of any commercial importance. Small quantities of ferro-tantalum have been prepared for use in the steel industry by the reduction of a mixture of tantalite and iron in the electric furnace, but the alloy does not seem to be widely used (see L. Guillet, *Comptes rend.*, 1907, 145, 327).

At the present time (April 1914) ferro-tantalum is sold in the United Kingdom for use in the steel industry at 7s. 6d. per lb. of tantalum contained. The alloy usually contains from 60 to 70 per cent. of tantalum.

A recent account of the uses of tantalum in science and technology is given by A. R. Meyer in *Dingler's Polytech. Journ.*, 1913, 328, 292.

## NIOBIUM

As mentioned on p. 55, this element, in the form of its oxide, is almost invariably associated with tantalum ores, but, at the present time, there appears to be no commercial use for the metal or its salts.

It can be obtained in a metallic state by several processes, amongst which may be mentioned—(1) Electrolysis of potassium fluoxy-niobate in a manner similar to that employed in the production of tantalum (see p. 57). (2) By passing a mixture of the vapour of the tetrachloride and hydrogen through a red-hot tube. (3) By the aluminio-thermic process, which yields a product containing about 3 per cent. of aluminium which can be removed by heating *in vacuo*. (4) By von Bolton's process of mixing niobium pentoxide with paraffin wax, squirting into fine threads, and heating these *in vacuo* to a temperature of 1,900° C. (see p. 58).

**Properties.**—Metallic niobium has a specific gravity of 12.7, and melts at 1,950° C. It is considerably less malleable and ductile than tantalum, and when in the form of powder it rapidly oxidises in air, but the massive metal is more resistant, probably owing to a protective coating of oxide being formed. It is insoluble in most acids, and is not attacked by *solutions* of the alkalis, but *fused* nitrates or alkalis readily attack the metal.

**Estimation of Tantalum and Niobium in Minerals.**—The complete analysis of a complex tantalum mineral is often a long, tedious, and complicated undertaking. It is impossible, in the space here available, to give full details of methods of analysis, but the following brief outline of a process for the separation and estimation of tantalum and niobium may be of service.

About 1 g. of the finely ground tantalite is fused for several hours with about five times its weight of potassium bisulphate, and after cooling, the melt is lixiviated with 5 per cent. sulphuric acid. The insoluble matter is separated by filtration and again fused. The sulphuric acid solutions thus obtained are diluted to 200 c.c., and, after nearly neutralising with ammonia, saturated with sulphur dioxide and well boiled for about one hour. This causes the precipitation of any traces of niobium and tantalum which may have passed into solution. The precipitate, together with the insoluble residue previously obtained, will now contain all the niobium, tantalum, silica, together with some of the tin, tungsten, and titanium. The moist precipitate is digested with ammonium sulphide in order to remove the tin and tungsten, and is then washed, transferred to a platinum basin, and dissolved in a few drops of hydrofluoric acid. After diluting the solution to about 20 c.c. it is boiled in order to expel silica. If the quantity of titanium present in the ore does not much exceed 5 per cent., then the niobium and tantalum in the hydrofluoric acid solution can be separated and estimated by the Marignac process, but if titanium is present in large quantity the separation is ineffective, and some other process must be adopted. The presence of titanium in tantalum ore also causes a large amount of the tantalum and niobic oxides to pass into solution after the fusion with potassium bisulphate, and special methods of analysis have to be adopted (see T. Crook and S. J. Johnstone, *Min. Mag.*, 1912, 16, 244). Assuming that only a small quantity of titanium is present, then the tantalum and niobium are separated as follows:—The solution in very dilute hydrofluoric acid is concentrated to about 20 c.c., heated to boiling, and to it is added a boiling solution containing about 0.7 g. of potassium fluoride. The solution is slowly evaporated to 10 c.c. and let cool slowly to about 15° C. When thoroughly cold, the clear solution, which contains all the niobium and a small part of the tantalum, is decanted through a small filter into a small platinum dish. The residual mass, consisting of crystals of potassium fluo-tantalate, is washed four times with a few c.c. of cold water, the washings being added to the main solution, which is evaporated to about 5 c.c. and let slowly cool. This solution is decanted and the crystals washed four times with a few c.c. of cold water, and then examined with a lens for flat plates of potassium fluo-niobate. If these are present they must be removed by further washing. Next evaporate the solution to dryness on the water bath, cool, add one drop of hydrofluoric acid and 0.1 g. of KF dissolved in 1 c.c. of water. Then run into the dish from 1 to 5 c.c. of water according to the proportion of niobium expected to be present, allowing 1 c.c. for each 7 per cent of  $\text{Nb}_2\text{O}_5$ . Heat rapidly for a few seconds, note the total bulk of solution, and set aside to cool for one hour. Filter the solution into a small platinum dish and wash the residue three or four times with a few drops of water, making note of the approximate bulk of the washings. To the solution add 8 c.c. of strong sulphuric acid, evaporate to fuming, and maintain at this temperature for at least twenty minutes in order to remove the last traces of hydrofluoric acid.

After cooling, the solution is poured into 150 c.c. of cold water, and the whole boiled for about twenty minutes in order to completely precipitate the niobium. The solution is filtered and the precipitate well washed with boiling water, dried, ignited, and weighed. The whole of the niobium and a small proportion of the tantalum is contained in this precipitate; the tantalum being allowed for on the following basis—0.00365 g.  $\text{Ta}_2\text{O}_5$  for each c.c. of solution from which the final crystallisation took place, and 0.00091 g.  $\text{Ta}_2\text{O}_5$  for each c.c. of wash water in the final filtration. The remainder of the tantalum is recovered by dissolving the crystallised potassium fluo-tantalate in a few c.c. of water, adding about 10 c.c. of concentrated sulphuric acid, and evaporating to fuming. When cold, the acid solution is poured into about 200 c.c. of water, and the tantalum precipitated by the addition of ammonia. The precipitate is filtered, washed, ignited, and weighed as  $\text{Ta}_2\text{O}_5$ .

A convenient and rapid process for the volumetric estimation of niobium in a mixture of oxides of niobium and tantalum has been described by F. D. Metzger and C. E. Taylor (*Zeits. anorg. Chem.*, 1909, 62, 382). The method depends on the fact that if succinic acid be added to a bisulphate fusion of niobic and tantalum oxides, the solution can be diluted and heated without depositing insoluble compounds of the two elements. When this solution is treated with amalgamated zinc, the niobium is reduced and can be titrated with potassium permanganate. About 0.5 g. of the mixed oxides is fused with 5 g. of potassium bisulphate, 10 c.c. of concentrated sulphuric acid added, and the heating continued until a clear solution is obtained. The solution is poured into a beaker, the crucible rinsed out with 30 c.c. of sulphuric acid, and the whole allowed to cool. Two g. of succinic acid are stirred into the liquid, followed by 20 c.c. of a saturated aqueous solution of succinic acid, and lastly, 200 c.c. of water. The liquid is heated to 75° C., and sent through a Jones zinc reductor (previously warmed by running through it 200 c.c. of 5 per cent. sulphuric acid at 75° C.), filled with 20 per cent. sulphuric acid also heated at 75° C. The niobium solution is followed, first by 50 c.c. of 20 per cent. sulphuric acid, and then by 200 c.c. of 5 per cent. sulphuric acid (both at 75° C.). The brown reduced solution and washings are at once titrated with potassium permanganate in an atmosphere of carbon dioxide. Under these conditions, niobic oxide is reduced to an oxide approximating to the formula  $\text{Nb}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ , whilst tantalum oxide is unaffected.

The degree of amalgamation of the zinc in the reductor is important. It is best prepared by shaking 600 g. of sieved zinc for several minutes with 250 c.c. of a solution containing 0.5 g. of mercury dissolved in 25 c.c. of concentrated nitric acid. The amalgamated zinc is washed first with water and then with dilute sulphuric acid, and is stored under water.

**Acknowledgments.**—Thanks are due to Messrs Siemens Brothers Dynamo Works for information on the recent utilisation of metallic tantalum, and to Messrs G. Blackwell & Sons of Liverpool for supplying quotations for tantalum ore and its ferro-alloy.

## CHAPTER V

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Tungsten



## CHAPTER V

# TUNGSTEN

### LITERATURE

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TUNGSTEN, like several of the rarer elements, was little more than a scientific curiosity up to about fifteen years ago, but its employment first in the steel industry, and more recently, in a ductile form for the manufacture of filaments for incandescent electric lamps, has led to the production of the metal in large quantities.

### Natural Occurrence

Tungsten ores are usually found in veins in the older plutonic rocks, or in the alluvium resulting from the denudation of these, being present in many tin deposits. The ores of commercial importance, at the present time, are **wolframite**, **hübnerite**, **scheelite**, and **ferberite**.

**Wolframite**, or wolfram, is a tungstate of iron and manganese, having a specific gravity of 7.2 to 7.5, and varying in colour from dark greyish to brownish black.

**Hübnerite** may be described as a variety of wolframite in which most of the iron has been replaced by manganese. It varies in colour from brownish to black, and usually occurs in bladed form.

**Scheelite**, a tungstate of calcium, is a white mineral having a specific gravity of 5.9 to 6.1, and when pure contains 80.6 per cent. of tungstic oxide ( $\text{WO}_3$ ).

**Ferberite** is a black opaque mineral having a specific gravity of about 6.8. It consists essentially of iron tungstate.

Other tungsten minerals of less importance are **cuprotungstite**, **stölzite** (lead tungstate), **tungstic ochre**, etc.

**Analyses** of some typical tungsten ore concentrates are given in the following table:—

TABLE XVI.

	Formula.	1.	2.	3.	4.
		Wolframite, N.W. Spain.	Scheelite, Zinnwald.	Hübnerite, Colorado.	Ferberite, Nederland.
		Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tungstic oxide	$\text{WO}_3$	64.13	77.84	70.21	63.88
Stannic oxide	$\text{SnO}_2$	0.68	...	...	...
Ferrous oxide	$\text{FeO}$	10.88	...	2.03	20.44
Ferric oxide	$\text{Fe}_2\text{O}_3$	...	...	...	0.35
Alumina	$\text{Al}_2\text{O}_3$	5.32	...	0.56	2.19
Manganous oxide	$\text{MnO}$	6.42	...	21.72	0.37
Lime -	$\text{CaO}$	1.21	19.48	0.37	0.35
Magnesia	$\text{MgO}$	3.16	...	...	0.50
Molybdic oxide -	$\text{MoO}_3$	...	2.23	...	...
Silica	$\text{SiO}_2$	7.71	...	4.91	6.45

1, 3, 4. O. J. Steinhart, *Min. Ind.*, 1908, 17, 830. 2. Traube, *Jb. Min.*, 1890, 7, 232.

### Geographical Distribution of Tungsten Ores

The increase in the demand for tungsten ore during recent years has led to the development of deposits in many countries, and it is impossible in the space available to give even a brief account of the more important of these. At the present time the most important producing countries are the **United States**, **India** (Burma and Shan States), **Queensland**, **New South Wales**, **Portugal**, **Argentina**, and the **United Kingdom**. An account of the occurrences in the United States will be found in the *Mineral Resources of the United States*, 1910, Part i., p. 744 (United States Geol. Sur., Washington, 1911). For a description of the other occurrences the literature quoted at the beginning of this article should be consulted.

**Concentration of Ore.**—Tungsten ore, which often occurs associated with numerous other minerals, is usually separated from these and concentrated by some process of wet dressing. This treatment results in the concentration of the tungsten ore, but the other heavy minerals present accumulate with it, and other means have to be adopted to separate these from the ore, in order to produce a marketable product. As wolfram ores are usually slightly magnetic, this removal can often be accomplished by means of an electro-magnetic separator (see Fig. 3.).

Owing to various causes, such as the excessive production of slimes, the losses in dressing tungsten ore are usually high.

### Production of Tungsten Ore

The following table shows the production, in short tons (2,000 lb.), of tungsten ores during recent years. For purposes of comparison the outputs from the various countries have been reduced to a basis of ore containing 60 per cent. of tungstic oxide,  $\text{WO}_3$  (*Min. Res. United States*, 1912, Part i., p. 993).



TABLE XVII.

	1908.	1909.	1910.	1911.	1912.
<i>Asia—</i>					
India	...	7	430	1,119	2,095
Federated Malay States	83	99	105	205	275
Japan	220	292	275	287	215
<i>Australasia—</i>					
New South Wales	269	431	413	512	298
Northern Territory	40	49	78	71	...
Queensland	516	679	1,145	750	944
Victoria	3	15	31	33	...
Tasmania	5	20	75	86	87
New Zealand	87	78	187	184	...
<i>East Indies</i>	25	24	33	...	29
<i>Europe—</i>					
Austria	44	43	54	50	...
United Kingdom	261	421	307	298	216
France	124	55	33	...	...
Germany	46	106	105	89	...
Portugal	684	609	1,132	1,078	1,466
Spain	249	142	169	106	...
<i>America—</i>					
United States	671	1,619	1,821	1,139	1,330
Argentina	548	900	826	683	702
Bolivia	187	168	232	370	547
<i>South Africa</i>	40	16	...	...	...

### Commercial Value of Tungsten Minerals

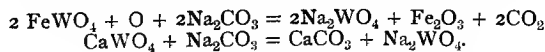
The price obtainable per lb. of tungstic oxide in the ore varies largely with the percentage of tungsten present. Thus, in the United States, in 1912, the ores were sold on the following scale (only a few of the prices are quoted):—

Tungstic Oxide in the Ore.	Price per Lb. of WO <sub>3</sub> .
Per Cent.	d.
10-14	10
35-39	14
50-54	16
60	19

### Manufacture of Metallic Tungsten and its Salts

Although the processes employed for the production of metallic tungsten from the concentrated ore do not appear to be very complicated, great care is necessary, at every stage, in order to avoid heavy losses of valuable material.

The present day method usually employed for the production of sodium tungstate from the ore is practically identical with the "Oxland" process which was patented in 1847. If bismuth is present, the ore is first roasted and then leached with hydrochloric acid. The dry finely powdered ore is heated in a reverberatory furnace with a quantity of sodium carbonate, equivalent to an excess of about 10 per cent. over the amount required to combine with the tungstic oxide in the ore to form sodium tungstate in accordance with the following equation—



About 10 per cent. of sodium nitrate is sometimes also added to the mixture. Whilst in the furnace, the mass is maintained at a red heat for about four hours, care being taken that it does not fuse, and only reaches a pasty condition. According to G. Erhard (*Die Metallurgie*, 1912, 9, 441), who gives a good review of the processes available for smelting tungsten ore, it is advisable to let the pasty mass cool after this first heating, crush in a ball mill, and again sinter. The first heating converts about 70 per cent. of the tungsten into sodium tungstate, whilst the second sintering increases this amount to about 90 per cent. After the second heating, the pasty mass is removed from the furnace and leached with water in superimposed vats, so that the weak liquor from the final washing of one batch is used for the first leaching of the next. The solid residue from this treatment often contains cassiterite (tinstone), which, being of considerable value, is recovered by treating the material on shaking tables of the Wilfley type (see Fig. 1.), or by other suitable means.

The solution obtained as above can be (1) evaporated to dryness to give crude sodium tungstate, or (2) evaporated to crystallisation for the production of the **pure salt**. The chief impurities present in the crude sodium tungstate produced by evaporation to dryness are:—Sodium sulphate, sodium silicate and arsenate, whilst iron and manganese occur in smaller amounts. When the pure salt is required, these impurities are removed by the following series of operations. Iron, manganese, and arsenic are precipitated by the addition of a small quantity of caustic soda, and the greater proportion of the sodium sulphate will crystallise out before the sodium tungstate. The silica passes to the mother liquor which remains after the crystallisation of the sodium tungstate, and may cause a considerable loss of tungsten, as it leads to the formation of soluble silico-tungstates. This loss is mitigated, to some extent, by the fact that this silico-tungstate can be obtained by further evaporation, and sold for fire-proofing purposes. It is also possible to recover the tungsten, thus retained by the silica, by adding a calcium salt to the solution, and thus precipitating calcium tungstate. After recrystallising the sodium tungstate and thus obtaining a fairly pure product, it is dissolved in boiling water, and added to a boiling solution of hydrochloric acid, which has been previously diluted with its own volume of water. This latter solution sometimes contains, in addition, about 6 per cent. of nitric acid. This treatment causes the tungsten to be precipitated in a granular form as hydrated tungstic oxide ("tungstic acid") which is filtered off and well washed in filter presses. In the precipitation and washing considerable losses may occur owing to the formation of a soluble acid tungstate, and also of colloidal tungstic acid, which pass away in the wash waters. The extent of these losses is influenced by (1) the strength of the solutions of sodium tungstate and hydrochloric acid before mixing; (2) the method of mixing, filtering, and washing. It is best to mix the solutions slowly, with constant agitation, at as high a temperature as possible, and to wash rapidly with dilute acid.

It is very essential that the tungstic acid should be washed free from sodium salts, for if this is not done the product, when dry, has a greenish tinge, and is supposed to be less suitable for the production of tungsten powder. Various other processes have been suggested for the production of sodium tungstate, amongst which may be mentioned that of Jean, which consists in heating the ore with calcium carbonate and sodium chloride, a process which is only applicable to pure wolframite. The Kempen Electro-Chemical Company heats sodium bisulphate to fusion with mono-hydrated sulphuric acid, and then introduces the powdered mineral (German Patent, 149,556, of 1902).

**Preparation of Metallic Tungsten.**—Metallic tungsten can be obtained from tungstic oxide by several processes, such as—(1) Reduction by means of hydrogen. (2) Heating with carbon in an electric furnace. (3) Heating with metallic zinc. (4) Conversion to the hexa-chloride and reduction in hydrogen. (5) Conversion to the nitride and heating. (6) Heating to redness a mixture of ammonium tungstate and metallic zinc. (7) Reduction with aluminium or magnesium. (8) Electrolysis of the double chloride of sodium and tungsten.

Few of these processes are of commercial importance, except (1) and (2), although certain of the others may be in use on a small scale.

Reduction in a current of hydrogen gives a purer product than that obtained when carbon is the reducing agent, but it is somewhat difficult to control the operation and to make the reaction go to completion. The reduction with carbon is, therefore, the process more usually employed. In practice, the dried tungstic oxide is mixed with slightly less than the full quantity of carbon required for its reduction by means of carbon monoxide, and the mixture heated in crucibles. The process, as described by G. Erhard, consists in mixing 100 kilos. of dried tungstic oxide with 14 kilos. of pure charcoal (petroleum coke) and 2 kilos. of rosin. This mixture is placed in a crucible, the lid firmly luted on, and the whole maintained at a temperature of 1,400° C. for some time.

The metallic powder produced, which is mixed with unburnt carbon and unreduced tungstic oxide, is elutriated so as to remove these, together with the very finest particles of metal. The material so removed is mixed with the next charge to be reduced.

**Cost of Production.**—The manufacturing costs in the production of metallic tungsten are somewhat high, owing to the number of operations, each of which entails some loss of material. For example, it is found that although from theoretical considerations 127 parts of the oxide should yield 100 parts of the metal, in practice at least 140 parts is required. The costs of production ("returning charge") per ton of metal amounts to about £80, so that if ore containing 60 per cent. of tungstic oxide costs £100 a ton, the metal will cost about £310 a ton.

**Ferro-Tungsten.**—This alloy, which finds a wide use in the steel industry, can be prepared by several methods, such as—(1) The direct reduction of the ore by means of carbon in a crucible. (2) By reducing in the electric furnace by means of some substance other than carbon. (3) By direct reduction in the electric furnace by means of carbon.

In the first process the concentrated ore is placed in a clay-lined crucible, together with a suitable flux and the reducing agent, and the whole is heated in a gas-fired furnace, together with the correct proportion of iron or steel scrap.

When direct reduction by means of carbon in the electric furnace is employed, wolframite, small hübnerite, and ferberite are easily reduced, but scheelite is more difficult to treat, and gives thick pasty slags. The alloys produced by either of the above processes are decarburised by means of refining slags.

The composition of tungsten powder and ferro-tungsten is shown in the following table, the powder being produced by the reduction of tungstic oxide by means of carbon, whilst the ferro-tungsten was obtained by reduction in the electric furnace (analyses quoted by O. J. Steinhart, *Min. Ind.*, 1908, 17, 833).

TABLE XVIII.

	Formula.	Tungsten Powder.		Ferro-Tungsten.		
		Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Tungsten	W.	97.02	98.63	85.15	79.48	71.80
Iron	Fe	0.61	0.59	14.12	18.60	24.35
Carbon	C	0.32	0.12	0.45	1.49	2.58
Silicon	Si	0.72	0.32	0.13	0.16	0.36
Manganese	Mn	0.16	...	0.085	0.21	0.078
Phosphorus	P	<i>Nil</i>	...	0.018	0.017	0.008
Sulphur	S	<i>Nil</i>	...	0.021	0.016	0.02
Aluminium	Al	0.47	0.21	...	0.001	0.07
Copper	Cu	...	...	...	...	0.008
Magnesium	Mg	0.32	...	...	...	...

At the present time (April 1914) ferro-tungsten containing about 80 per cent. of tungsten and a maximum carbon content of one per cent., is sold, in the United Kingdom, at 2s. 9d. per lb. of tungsten contained.

**Ductile Tungsten.**—The advent of the tungsten metal filament lamp (see p. 79) led to a search for methods of producing the metal in a more ductile form than it had previously been obtained, and it was found that the pure metal, when submitted to repeated swaging and heating, loses its crystalline character and becomes ductile and fibrous.

The master patent in this connection appears to be English Patent 23,499 of 1909, granted to the British Thomson-Houston Company, which is briefly as follows. By repeatedly working a heated body of coherent tungsten, the metal may be obtained in a form which is ductile both when hot and at ordinary temperatures; the consolidated rod being transformed by repeated rolling, hammering, swaging, or drawing, into a form which shows a conchoidal fracture and ultimately becomes very fibrous. This process is described in full on p. 81.

For the production of ductile tungsten by the above method, it is necessary that metal of great purity should be employed. According to O. Ruff (*Zeits. angew. Chem.*, 1912, 25, 1889), the metal must be entirely free from oxide; iron and nickel and non-metallic impurities, such as sulphur, phosphorous, etc., must be entirely absent. It should not contain more than about 0.1 per cent. of carbon. Before working, the metal should be sintered almost to the melting point in order to obtain it in as dense a condition as possible. In order to get a pure metal, it is desirable to purify the trioxide by reducing it to the dioxide, volatilising the latter as oxychloride, and treating this with hydrochloric acid. Tungsten dioxide ( $\text{WO}_2$ ) can be prepared by heating the trioxide to bright redness with one-fifth of its weight of glycerol or similar hydroxy compound (English Patent, 18,922, 1907). By this means silica and phosphoric acid are left behind in the non-volatile residue, whilst arsenic and antimony pass into solution in the hydrochloric acid. The pure trioxide is reduced in a rapid current of hydrogen at a temperature of  $1,250^\circ \text{C.}$ , and is pressed into rods which are hardened by heating in hydrogen to a temperature of about  $1,300^\circ \text{C.}$ , and then sintering in a special furnace at about  $2,650^\circ \text{C.}$

It is sometimes necessary, in the case of very pure tungsten, to add about 0.05 per cent. of carbon in order to lower the melting point. Other methods for producing ductile tungsten are described in Chapter VI., p. 81.

**Properties of Metallic Tungsten.**—Cast tungsten, or that in the form of powder, has properties differing widely from those of the pure wrought metal, such as is used in the manufacture of incandescent electric lamp filaments (see p. 79). The powder is a hard, brittle, crystalline substance having a specific gravity of 16 to 17. The **pure metal** is a much softer and tougher material which may be rolled into thin sheets, welded at a yellow heat, and drawn into exceedingly fine wire. It has a melting point of about  $3,080^\circ \text{C.}$ , and a specific gravity of 18.8. In common with most metals, its tensile strength increases with the thinness of the wire tested. Thus, a wire 5 mm. in diameter has a tensile strength of 460,000 lb. to the square inch, whilst that of wire of 1.2 mm. in diameter is 580,000 lb. per square inch. Air and water, at ordinary temperatures, are without effect on metallic tungsten, but at a red heat the metal is oxidised. Molten sulphur and phosphorous attack it slowly, but it is rapidly converted to sulphide or phosphide by their vapour. Fused nitrates, peroxides, potassium bisulphate, alkali carbonates, and caustic alkalies readily attack the metal, but solutions of these are without action. The metal is unattacked by boiling dilute sulphuric acid, but the concentrated acid attacks it slowly. Strong or weak hydrochloric acid has no action at ordinary temperatures, but the strong acid, at the boiling point, slowly attacks the metal, producing a black coat of oxide. Concentrated nitric acid or hydrofluoric acid have little action separately, but the metal is rapidly attacked by a mixture of these two acids.

### Utilisation of Metallic Tungsten and its Salts

**Tungsten Steel.**—About 90 per cent. of the tungsten produced is used in the manufacture of tungsten steel. One of the most important properties of tungsten is the additional hardness and toughness which a small quantity of it is

capable of imparting to steel, and for this reason tungsten steel is of especial value for the construction of **armour plate, projectiles, and fire-arms**. Tungsten steel is also especially suitable for the manufacture of high-speed tools, which are required to retain their temper when run hot. A steel suitable for such use may contain tungsten, 8.5 per cent. ; chromium, 4.0 per cent. ; carbon, 1.25 per cent.

**Self-hardening steels**, *i.e.*, those requiring no tempering after forging, may have a composition between the following limits—Tungsten, 2.4 to 3.4 per cent. ; chromium up to 6 per cent. ; carbon, 0.4 to 2.2 per cent. ; silicon, 0.2 to 3.0 per cent.

The chief characteristics of tungsten steels are that they possess a tensile strength and elastic limit which, within certain limits, become higher in proportion as the percentage of tungsten increases. Their elongation, reduction of area, and resistance to shock diminish proportionately, whilst the hardness increases somewhat rapidly with the percentage of tungsten.

For use in the steel industry, tungsten is usually employed in this country in the form of its ferro-alloy, but the powdered metal is often employed abroad.

Tungsten is a constituent, to the extent of about 5 per cent., of an interesting alloy known as "Stellite," which contains, in addition, 75 per cent. of cobalt and 20 per cent. of copper. This alloy can be utilised for cutting tools, being very hard and non-rusting (see E. Haynes, *Bull. Amer. Inst. Min. Eng.*, 1913, 249, and United States Patents, 1,057,423 and 1,057,828, 1913). It also enters into the composition of the alloys "Minargent," "Platinoid," "Partinium," and "Sideraphit."

Numerous uses have been suggested for wrought and ductile tungsten. Its applications in the chemical industry are fairly obvious from a consideration of the properties quoted on p. 68.

It may also find numerous applications in electro-technology. Thus it is stated to be particularly suitable for contacts, such as those of magneto spark coils, signal relays, sending keys, etc., being much superior to platinum, or platinum-iridium, for these purposes. As the heat conductivity of tungsten is twice that of platinum, contacts made of the first-mentioned metal remain much cooler whilst in use than do those made of platinum. Owing to its higher melting point, tungsten is stated to be better than platinum as a target material for Röntgen ray tubes. For the numerous other uses which have been suggested for tungsten, the article by C. G. Fink should be consulted.

**Bronze Powders.**—When potassium tungstate is fused with pure tin, coloured compounds are produced, known as tungsten bronzes, which are largely employed for decorative purposes.

**Magenta Bronze** is produced by adding tungstic oxide to fused potassium carbonate until the solution is saturated. The product thus obtained is gently heated in hydrogen and then successively treated with water, hydrochloric acid, and potassium hydroxide solution. These operations yield a product in the form of small violet crystals, which have the composition  $K_2W_4O_{12}$ . Other alkali-tungstate bronzes are also employed for decorative purposes, owing to their colour and insolubility in acids. They can be prepared electrolytically by fusing together the calculated quantities of tungstic acid and metallic carbonate and then electrolyzing the mass. According to Philipps (*Ber.*, 1882, **15**, 499), the following tungsten-sodium bronzes are known— $Na_5W_6O_{18}$  (golden yellow);  $Na_2W_5O_{15}$  (blue);  $Na_2W_3O_9$  (red);  $Na_4W_5O_{15}$  (reddish yellow). Blue tungsten-lithium bronzes have been described by Hallopeau (*Comptes. rend.*, 1898, **127**, 512); also by G. von Knorre and E. Schäfer, (*Ber.*, 1902, **35**, 3,407). Other tungsten bronzes have been described; for accounts of these see E. Engels, *Zeits. anorg. Chem.*, 1903, **37**, 125, and Schäfer, *Zeits. anorg. Chem.*, 1904, **38**, 148.

In the **textile industry**, sodium para-tungstate is used to a small extent for the fireproofing of cloth and other fabrics, and as a mordant for calico printing. Tungsten salts are also used as mordants for silk, and have the additional advantage that they also serve as weighting materials.

Tungstic oxide is used in **glass and porcelain** manufacture for the production of yellow colours. Formerly, difficulties arose from the formation of an opalescence in the glaze, but a method has been described by which this may be avoided (see A. Granger, *Comptes. rend.*, 1905, **140**, 935).

Sodium tungstate is sometimes used for decolorising acetic acid.

### Estimation of Tungsten in Minerals and Salts

A process for the determination of tungsten in wolframite will serve to illustrate the methods employed (Treadwell and Hall, "Analytical Chemistry," vol. ii., p. 259). About 1 gm. of the extremely finely powdered mineral is fused with 4 gm. sodium carbonate in a platinum crucible for from one-half to three-quarters of an hour. After cooling, the melt is boiled with water and filtered. The residue contains iron, manganese, calcium, and magnesium, and sometimes small amounts of niobic and tantallic acids. The solution contains all the tungstic acid and silica. The aqueous solution of the alkali tungstate is treated with an equal volume of nitric acid and boiled until the precipitate becomes a pure yellow. After the precipitate has settled, the supernatant liquid is decanted through a filter and the precipitate washed three times, by decantation, with a mixture of equal parts of nitric acid (sp. gr. 1.2) and water, and finally upon the filter until the washings leave no residue when evaporated to dryness on platinum foil. Then, in order to remove nitric acid, the precipitate is washed twice with a neutral five per cent. solution of ammonium nitrate. By this means the greater proportion of the tungstic acid will be in the precipitate, but a small quantity will be in the filtrate, which is then evaporated to dryness, the residue moistened with ammonia, again evaporated to dryness, dissolved in as little water as possible, and treated with an equal volume of concentrated nitric acid. After boiling and filtering, the precipitate is washed as before. The two precipitates of tungstic acid are dried, ignited, and weighed as impure tungstic oxide ( $\text{WO}_3$ ); the impurities present being usually silica and stannic oxide. To remove silica, the oxide is treated with hydrofluoric and sulphuric acids, ignited, and again weighed. The stannic oxide may be removed by Rammelsberg's method of igniting the residue with pure dry ammonium chloride. For a full account of the numerous methods of separating tungsten from other metals see "Treatise on Quantitative Analysis," by J. W. Mellor (London, 1913), p. 405-411.

**Tungsten Bronzes.**—These salts are not readily decomposed by acids, but can be easily attacked by the method of Brunner (*Inaug. Diss. Zurich*. 1903). About 0.5 gm. of the finely powdered bronze is treated in a porcelain crucible with 2 gm. of alkali-free ammonium sulphate and 2 gm. of concentrated sulphuric acid, and carefully heated over a very small flame until vapours of sulphuric acid begin to escape. After a part of the ammonium sulphate has been volatilised, the mass is allowed to cool and further quantities of ammonium sulphate and sulphuric acid added. After further heating, the mass is allowed to cool, treated with water, and transferred to a porcelain dish. About 50 c.c. of concentrated nitric acid is next added and the contents of the dish digested on the water bath for three or four hours, after which it is diluted with water and the tungstic acid filtered off. The remaining treatment is similar to that already described above.

## CHAPTER VI

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# The Incandescent Electric Glow Lamp Industry





## CHAPTER VI

# THE INCANDESCENT ELECTRIC GLOW LAMP INDUSTRY

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### Incandescent Electric Glow Lamps

THE modern electric glow lamp may be briefly described as consisting of a glass bulb, enclosing a fine thread of some refractory substance, known as the filament, which, when heated by the passage of an electric current, will radiate light. The atmosphere in the bulb is usually reduced nearly to a vacuum, but occasionally a gas in a partially rarified condition is used.

The numerous problems involved in the manufacture of the various types of electric glow lamps are mostly of an electrical, rather than a chemical nature, and, therefore, cannot be fully discussed in this volume. Although great developments have taken place in the method of manufacture of the metal filament lamp (see p. 77), these lamps have by no means entirely displaced the carbon filament variety. As certain of the processes employed are very similar, both for the metal and carbon filament lamp, a very brief outline of the general method of manufacture of the latter is here given.

### Carbon Filament Lamps

The following description, which is an account of the process as employed at the works of the Edison & Swan United Electric Light Co., Ponders End, may be taken as being typical of the methods generally in use in this branch of industry.

The first operation is the production of the glass bulb which is to enclose the filament. This is made by first blowing an elongated bulb, which is given the finished shape by completing the blowing in a metal mould. For this purpose

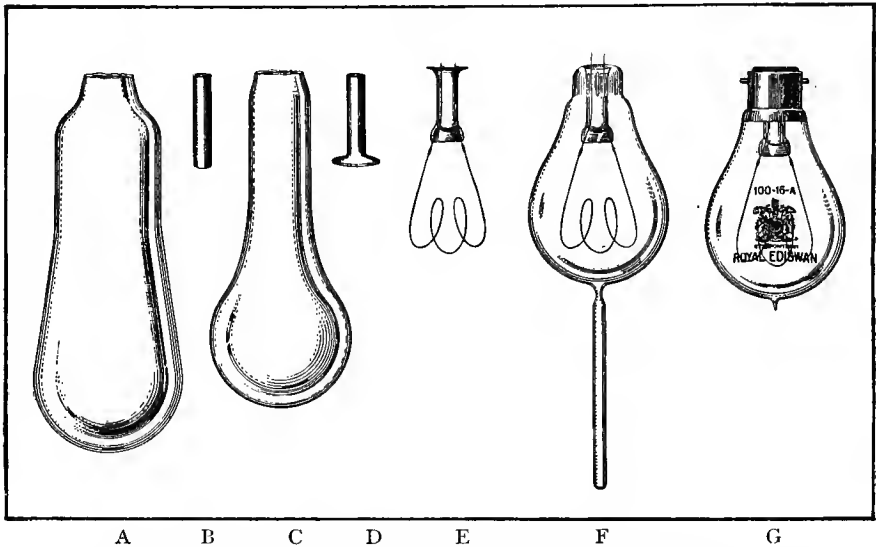


FIG. 24.—Stages in the Manufacture of a Carbon Lamp.

A and C show the bulb before and after it has been blown in the mould. B and D represent the tube for the leading-in wires before and after flanging. The filament attached to the leading-in tube and ready for sealing into the bulb is shown in E. The lamp ready for pumping is shown in F, whilst G represents the finished lamp.

the best flint glass containing a large percentage of lead is usually employed. The shapes thus produced are shown in A and C of Fig. 24. A small hole is next blown in the bottom of the bulb, and into it is sealed the piece of glass tubing which is required for use in the final operations of evacuating and sealing off the finished lamp. The two wires which in the finished lamp will convey the current from the mains to the filament are usually made in three sections (see Fig. 25). The first section, AB, is made of copper wire, whilst the second portion, BC, is composed of platinum or some alloy which has the same coefficient of expansion as the glass, in order that the joint between glass and metal may be perfectly gas tight. Alloys used for this purpose include ferro-nickel and "platinoid" (an alloy of copper, zinc, tungsten, and nickel). "Partinium" is also used, and consists of an alloy of tungsten, aluminium, tin, copper, and magnesium (English Patent, 21,573, 1895). The lower section, CD, which is joined to the filament, is often composed of nickel.

These wires are next sealed into the small glass tube D (Fig. 24), and are then ready to be attached to the filament, the method of making which will be described later. Several processes are in use for attaching the finished carbon filaments to the leading-in wires, the method selected being largely dependent upon the amount of shock which the lamp will have to withstand in use, and upon the strength of the current to be used in the lamp. For low amperage lamps, the joint between the filament and wires is effected by covering the junction with a special paste, the essential constituents of which are graphite and sugar. When an extra strong joint is required, the filament and

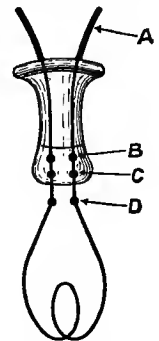


FIG. 25.—Connections between Filament and Leading-in Wires.

leading-in wires are brought into close contact, immersed in a liquid hydrocarbon, usually ligroin or benzene, and a current passed. This causes a small arc to play across the gap between the leading-in wires and filament, which decomposes the hydrocarbon and forms a compact deposit of carbon around the joint. The filament and its holder is now ready for sealing into its bulb, this operation being now usually done by machinery in most modern works. The lamp is now ready for exhausting, or "pumping," as it is called in the works. This operation is sometimes carried out in two stages, the bulk of the air being removed by means of a pump, and the evacuation completed by means of a Sprengel or similar type of pump.

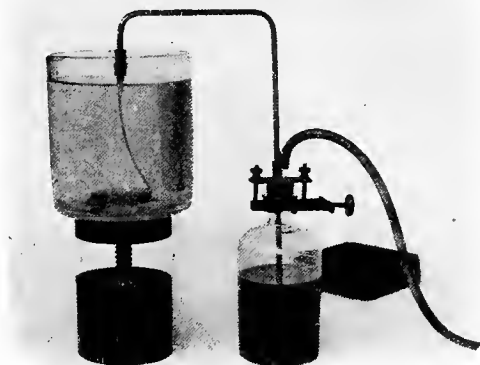


FIG. 26.—Squirting Carbon Filaments.

The degree of evacuation which is claimed for several modern types of pump is shown in the following table :—

TABLE XIX.

Pump.	Pressure left in Bulb.
	Mm.
Geisler - - - - -	0.0085
Sprengel (five tubes) - - - - -	0.000006
Geryk (oil pump) - - - - -	0.0002
Töpler (new type) - - - - -	0.00009

Carbon filament lamps are usually evacuated so as to leave a pressure of about 0.005 mm. in the bulb, and when the process is finished, the glass stem is melted and the tube sealed off close to the bulb. It next has its candle power tested photometrically, using electric lamp standards with the Lummer-Brodhun disc, and is then ready for fixing into its metal socket, which is done by means of a special paste composition consisting largely of plaster of Paris, together with a small quantity of gum. A small spot of solder on each of the terminals completes the lamp. The above is a very brief outline of the general method of manufacture employed; for full details the literature mentioned above should be consulted.

In most modern works, the whole of the above series of operations, with one or two exceptions, is carried out by machinery.

**Carbon Filaments.**—In the earlier types of lamp these were made of carbonised bamboo or cotton fibre, but at the present day they are made almost entirely from cotton wool, which is dissolved in a strong solution of zinc chloride to give a thick syrupy liquid. This dark greenish solution is squirted, by pressure, through various-sized nozzles which are immersed in jars of methylated spirit. As

the solution is forced from the jet, the cellulose is precipitated by the methylated spirit, and so forms a continuous filament. This operation is shown in Fig. 26.

The gelatinous filaments, thus produced, are removed from the solution and air-dried on frames. When dry, the filaments, which now resemble cat-gut, after being examined for defects, are passed repeatedly through drawplates until they are reduced to the requisite standard diameter. The filaments are next wound on porcelain or metal frames, which have the same shape as it is desired to give to the finished filament, immersed in graphite contained in crucibles, and raised to about  $2,000^{\circ}\text{C}$ . This latter process, which is known as "**metallising**," is sometimes repeated after the filament has been "**flashed**." By this means a filament of pure carbon of the desired shape is obtained, and after being carefully sorted, the selected filaments are submitted to the process of "**flashing**." This consists in



FIG. 27.—"Flashing" Room at Messrs Edison & Swan's Works.

electrically heating the filament to bright redness in a glass jar, having in it an atmosphere of a volatile hydrocarbon, such as ligroin or benzene, until it has attained a certain resistance, when the heating current is automatically cut off. The operation is usually conducted by considerably reducing the pressure of air within the jar and then admitting a definite volume of the hydrocarbon vapour. If the latter were used at atmospheric pressure, the deposition of carbon would be rapid, and an insufficiently dense layer would result. It is usual to employ a current about twice as great as that which will be used in the finished lamp. This process effects several improvements in the filaments, amongst which may be mentioned—(1) Carbon is deposited on the filament in a hard, lustrous condition, and in this form has a high light emissive power. (2) Any small inequalities in the thickness of the filament are levelled up, because the carbon is deposited least on those parts of the filament which have the least resistance, *i.e.*, those which are thickest. The flashing room at Messrs Edison & Swan's works is shown in Fig. 27.

The filaments are next graded according to their diameter and resistance, and are then ready for attaching to the leading-in wires by one of the processes which have been already described (p. 74).

### Metallic Filament Lamps

There are probably few articles in commerce whose introduction created such widespread interest and demand as the metal filament electric glow lamp.

Briefly summarised, the transition from the carbon filament to the present day metal filament lamp was as follows:—The carbon filament lamp with an efficiency of three watts per candle power was succeeded in turn by the “metallised” carbon filament having an efficiency of 2.5 watts, the tantalum with 1.7 watts, squirted tungsten requiring 1.25 watts, and the ductile or drawn tungsten lamp consuming 1 watt per candle power. More recently, however, the nitrogen-filled drawn tungsten lamp has been introduced, and has an efficiency of 0.5 watt per candle power (see p. 86).

The carbon filament lamp, in its many forms, had reigned unchallenged for many years when the first metallic filament lamp was made by Welsbach in 1898, as the outcome of his investigations on the use of metals having a high melting point as incandescent electric illuminants. It is rather interesting to note that the man who, by his invention of the incandescent mantle, put coal gas lighting on a competitive basis with electricity, should indicate the lines of development for the electric glow lamp, so that it might equal incandescent gas lighting in efficiency. The changes during the past ten years in the method of manufacture of metal filament electric lamps have been many and varied, and it is not possible to give here a full account of these. The following summary is, therefore, only intended to indicate briefly the more important stages through which the metal filament has passed in order to attain its present degree of efficiency.

In order that a metal may be suitable for use as a filament for incandescent electric lamps, it is essential that it should have a high melting point, be fairly ductile, and possess a low vapour tension under working conditions, whilst its radiation must be highly selective. It has been shown by C. W. Waidner and G. K. Burgess (*U.S. Bureau Standards*, 1907, 2, 319) that the light emitted by an incandescent metal varies as the twelfth power of the temperature, whilst the energy required varies as the fifth power of the temperature. It is seen, therefore, that a small increase in the working temperature of the filament is of considerable advantage.

The melting points of some of the metals which have been suggested or used as filaments are shown in the following table:—

Tantalum -	2,910° C.	Molybdenum -	2,450° C.
Thorium	over 1,700° C.	Zirconium -	about 1,300° C.
Tungsten	3,080° C.	Titanium -	1,795° C.

Amongst the advantages possessed by metal filaments over those of carbon is that, being good conductors of electricity, their resistance increases with temperature, whereas with carbon filaments increase of temperature causes a decrease of resistance, as the substance is a poor conductor of electricity. For this reason, fluctuations in voltage cause smaller alterations in the intensity of the light given by a metal filament than would be the case if a carbon filament were employed.

The first metal filament lamp constructed on modern lines was one introduced by Welsbach in 1898, the filament of which was composed of metallic **osmium**, one of the platinum group of metals (English Patent, 7,210, 1900).

This lamp had many disadvantages besides the high price of the metal, which was at that time about £100 per lb. The lamps had to be burned in a vertical position, otherwise the filaments sagged and broke, and they could not withstand shock. Low voltage lamps only could be produced, and therefore on the ordinary circuit several lamps had to be run in series. The filaments were first made by heating a platinum wire in an atmosphere containing a volatile osmium compound. This caused the deposition of metallic osmium on the wire from which the platinum was subsequently volatilised by increasing the temperature. At a later date, filaments were also made by the “squirting” process, and a lamp having a filament of metallic osmium was on the market, for a short time, under the name of the “**Osmi**” lamp. The physical properties of the earlier types of osmium filament lamps have been described by F. G. Bailey (*Electrician*, 1904, 52, 646). The patent literature indicates that the idea of using osmium as a filament has not been entirely abandoned (see United States Patents, 1,090,111; 1,109,886 of 1914).

After Welsbach had thus indicated the direction in which improved efficiency of the incandescent electric lamp was to be sought, there were numerous attempts

to utilise, as filaments, other metals of the platinum group, either alone or alloyed with base metals in order to reduce the tendency towards volatilisation. After numerous trials, however, the metals found to be most suitable were tantalum and tungsten, neither of which is a member of the platinum group. At the outset, considerable difficulty was experienced in producing filaments of sufficient strength and thinness, and it was soon realised that the filament drawn from a rod of ductile

metal had many advantages over one made by the squirting process, as then used (see pp. 75 and 80).



FIG. 28.—  
"Spider."

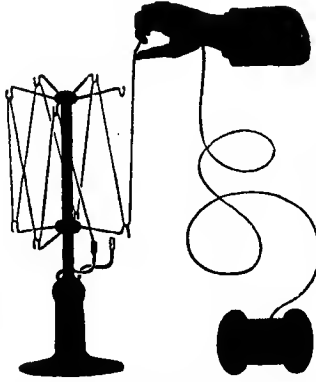


FIG. 29.—Method of Arranging  
Continuous Filament on "Spider."

**The Tantalum Lamp.**—The first lamp placed on the market having a filament of drawn wire was the tantalum lamp, which was introduced in 1903 by the Siemens & Halske A. G. of Charlottenberg, Germany. The earlier tantalum lamps had filaments varying in diameter up to 0.28 mm., but with the improvement in the method of making the metal more ductile, it was found possible to make wire having a diameter of less than 0.02 mm. This improvement permitted of the production of lamps suitable for use on a current of any voltage

commonly employed, but led to a difficulty in accommodating a long length of wire within a bulb of such a size as would be practicable to use. As tantalum has a much lower specific resistance than carbon, tantalum filaments have to be two and a half times the length and one quarter the diameter of carbon filaments for equal voltage and candle power. Thus, a tantalum filament for a 110 volt, 25 candle power lamp is 645 mm. long and 0.047 mm. in diameter, whilst a carbon filament for a lamp of similar voltage and candle power would be about 250 mm.

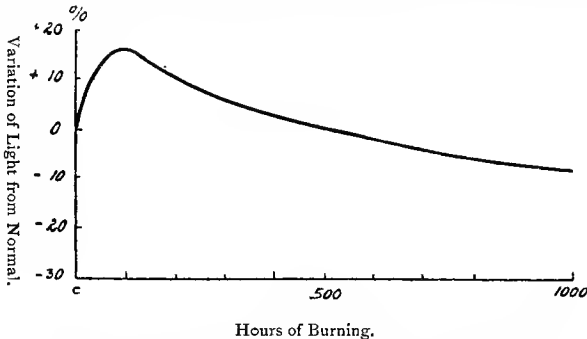


FIG. 30.—Variation of Luminosity of the Tantalum Lamp.

long and 0.18 mm. in diameter. The fact that the working temperature of the tantalum filament was very near to its softening point precluded the use of the double loop sometimes employed in carbon filament lamps, but this difficulty was surmounted by the invention of the "Spider" shown in Fig. 28 (German Patent, 153,328). The method of arranging the filament in zigzag fashion on the spider, as shown in Fig. 29, permits of the lamp being burned in any position.

Tantalum lamps have an initial efficiency of about 1.5 watts per (Hefner) candle power, the light intensity increasing slightly during the first fifty hours of use, and then decreasing slowly (see Fig. 30). The consumption of current per candle power

slowly increases with the time that the lamp has been in use (see Fig. 31). The light intensity of the tantalum lamp varies by about 4 per cent. for each 1 per cent.

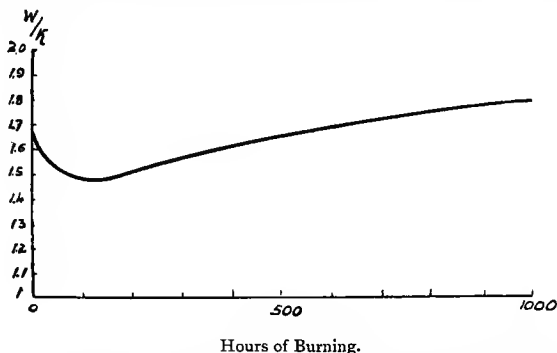


FIG. 31.—Variation in Consumption of Current of Tantalum Lamp.

difference in voltage at the lamp terminals. The variations in candle power caused by alterations in the voltage are shown in the following table :—

TABLE XX.

Variation in Pressure. Per Cent.		Candle Power.					Average Candle Power as Per Cent. of Normal.	Watts per Hefner* Candle Power.
Below normal -	{ - 20	3.9	6.3	9.9	12.6	19.7	39.4	2.60
	{ - 15	5.0	8.0	12.5	16.0	25.0	50.0	2.25
	{ - 10	6.5	10.3	16.1	20.6	32.2	64.5	1.95
	{ - 5	8.1	13.0	20.3	26.0	40.5	81.0	1.70
Above normal -	{ + 5	12.2	19.5	30.5	39.0	60.9	121.9	1.35
	{ + 10	14.7	23.6	36.8	47.2	73.6	147.2	1.20
	{ + 15	17.5	28.1	43.8	56.2	87.7	175.5	1.10
	{ + 20	20.7	33.2	51.8	66.4	103.8	207.5	1.00
Normal pressure	...	10	16	25	32	50	100	1.50

The initial increase in the light intensity may be due to a structural change in the filament, which causes a decrease in its resistance. When examined under the microscope, a tantalum filament, which has been burnt for some time on a direct current circuit, shows a tendency to contract into drops (see Fig. 32). The alternating current, under similar circumstances, causes a disconnected appearance in the filament (see Fig. 33). As would be expected from these observations, tantalum lamps when used on alternating current circuits have a somewhat shorter life than when a direct current is employed.

The tantalum lamp met with great success during its early days, about 103 million lamps being sold during the years 1905-1911.

**The Tungsten Lamp.**—The drawn wire tantalum lamp was followed by numerous patents for utilising metallic tungsten as a filament. Owing to the hardness and brittle character of the metallic tungsten at that time produced, the process of making filaments by drawing the metal, in the same way as tantalum was drawn, could not be employed. The filaments, therefore, had to be produced

\* The Hefner candle-power is equal to about 1.13 British standard candles.

by a "squirting" process, similar to that employed in the manufacture of carbon filaments, or by producing a coating of tungsten on a core of carbon or other refractory substance.

The many processes which have been employed up to the present day may be roughly classified into those involving—(1) Substitution. (2) Amalgamation. (3) Squirting a paste containing tungsten powder. (4) Squirting colloidal tungsten. (5) Drawn wire. (6) Alloy processes.

In the first-mentioned method, which is covered by French Patent, 347,661 of 1904; English Patent, 11,949 of 1905; German Patent, 184,379 of 1905, metallic tungsten powder is mixed with an organic binding material, such as gum, and squirted into filaments. The carbon is eliminated by placing the filaments in an atmosphere containing a volatile compound of tungsten, such as the oxychloride, and a small quantity of hydrogen. When the filament is heated to redness by the passage of an electric current, tungsten is substituted for carbon.

A typical example of the second-class of process is one patented by the General

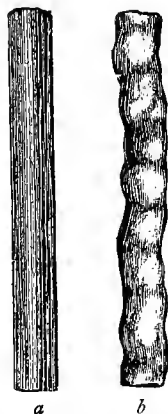


FIG. 32.—Tantalum Filament  
(a) before and (b) after Use  
on Direct Current Circuit.



FIG. 33.—Tantalum Filament  
after Use on Alternating  
Current Circuit.

Electric Company of the United States. The method consists in mixing metallic tungsten powder with an amalgam containing equal amounts of cadmium and mercury, and squirting the mixture through a die in the usual way. The cadmium and mercury in the filament, thus produced, are subsequently volatilised by heat, and the filament remaining has the usual brittleness, but it is claimed that after moderate heating it becomes pliable and can be bent to any desired shape (see English Patent, 18,745 and 18,748 of 1906, and 5,576 of 1907).

In the third type of process, as in the other classes, numerous modifications have been employed. Thus the binder may be one which, on heating, leaves a carbonaceous residue, *e.g.*, gum, sugar, gelatine, or nitro-cellulose dissolved in amyl acetate. On the other hand, it may consist of some substance which, although acting as a binding agent at ordinary temperatures, is volatilised, on heating, without carbonising. Examples of this class of binder are paraffin wax, camphor, and pinene hydrochloride. Binders of this class are employed in the paste process patented by Just, in which filaments are made by mixing a noncarbonising binding agent with a compound of tungsten which is reducible by hydrogen. After pressing and drying, the filaments are reduced in hydrogen at such a temperature that the



binder is volatilised. The process avoids the difficulty experienced in completely removing the carbon which is deposited when the other class of binder is used.

In certain processes, *e.g.*, French Patent, 357,842 of 1905; German Patent, 182,683 of 1905, finely powdered metallic tungsten is mixed with an organic binding material and the paste squirted into threads, which, after drying in a non-oxidising atmosphere, are ignited by passing an electric current through them in an atmosphere of a reducing gas consisting chiefly of hydrogen.

The use of tungstic oxide in squirted filaments is covered by English Patent, 18,814 of 1905, and French Patent, 357,868 of 1905.

Tungstic oxide for the production of squirted filaments can be prepared, in a suitable condition, by boiling hydrated tungstic oxide with ammonia until crystallisation occurs. The crystals are removed, heated to 250° C. for some time, and the residue boiled with water until it changes to a viscous plastic mass, which is then ready for squirting into filaments (French Patent, 379,069 of 1907). According to some authorities, the violet oxide of tungsten ( $W_2O_5$ ) or the brown oxide ( $WO_2$ ), are more suitable for the manufacture of filaments, as they conduct electricity better at ordinary temperatures than does the yellow oxide ( $WO_3$ ).

According to English Patent, 14,850 of 1908, plastic tungstic acid, suitable for the preparation of filaments, can be made by treating the hydrated oxide with ammonia at -20° C.

**Colloidal Tungsten Filaments.**—One of the most successful of the squirting paste processes is that in which colloidal tungsten is employed. The feature of the process is that, owing to the plastic and coherent nature of the material, no binding material is required; a much stronger filament being thus produced, and the difficulty of removing the carbon from the filament is avoided.

The use of many colloidal metals for the production of lamp filaments is covered by English Patent, 28,154 of 1904, with numerous additions granted to Dr Kuzel. The metals mentioned in the master patent include tungsten, uranium, molybdenum, vanadium, tantalum, nickel, titanium, thorium, zirconium, platinum, osmium, iridium, and silicon.

Colloidal tungsten may be prepared by allowing an electric arc to play between roughened electrodes of tungsten under water, or by the methods of Wedekind or Wright. The finely divided colloidal tungsten can be separated from the water by slow evaporation, and the plastic mass, thus obtained, is squirted into filaments. At ordinary temperatures the filaments, thus obtained, do not conduct electricity at low voltages, but when heated to 60° C. they conduct sufficiently well to enable the final drying and sintering of the filament to be carried out. The preliminary heating to 60° C. can be dispensed with if a current of 400 to 1,000 volts be used for performing the operation (English Patent, 12,968 of 1908). In order to avoid small cavities in the filament, the heating is carried out in a non-oxidising atmosphere, the pressure of which is reduced to at least 150 mm., and preferably to 40 mm. During the operation a continuous current of gas, consisting of about 80 per cent. nitrogen and 20 per cent. hydrogen, is passed through the apparatus. As the temperature is gradually increased the tungsten returns to its massive state, and the filament decreases considerably in size and resistance.

Colloidal tungsten filaments have been produced in large quantities, but the process is now replaced, at one large works at least, by a process in which colloidal tungsten is used together with certain of the rare earth metals (see "Tungsten Alloy Filaments" p. 84).

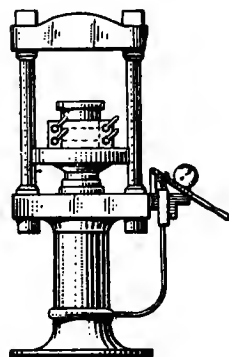


FIG. 34.—Hydraulic Press and Mould.

**Drawn Wire Tungsten Filaments.**—The manufacture of drawn filaments from metallic tantalum has already been mentioned on p. 57. The production of drawn tungsten filaments was rendered possible by the discovery of a method of producing ductile tungsten introduced by the General Electric Company of the United States. The general principles involved in the method have been already

described on p. 68; the actual details of the various operations are not disclosed by those working the patents. The following description, from *La Technique Moderne*, 1914, 6, 193, through the *Electrical Review*, 1914, 74, 595, gives an account of the essential details of the process.

Pure metallic tungsten is very fragile at forging temperature, but at a white heat it can be hammered, rolled, or drawn, and so be rendered malleable. In order to obtain the metal in this condition, it must be free from oxide, iron, nickel, and contain only traces of sulphur, phosphorus, antimony, arsenic, selenium, or tellurium, whilst the carbon content must not exceed 0.05 per cent. The heating must be performed very gradually, and it is necessary to protect the metal from contact with air during the various stages of its manufacture. The operations may be roughly divided into six sections.

1. *The Production of Pure Metallic Tungsten.*—This is effected by heating pure tungstic oxide, prepared by one of the methods already described (see p. 66), in a current of pure hydrogen at a temperature of about  $1,000^{\circ}\text{C}$ .

2. *Agglomeration of the Tungsten Powder into Bars.*—This is effected by means of a hydraulic press, exerting a pressure of about 5,000 kilos per square centimetre (see Fig. 34). The bars, which are about 130 mm. long and 4 mm. thick, are exceedingly fragile, and their formation requires considerable skill. The powder used in this process should be of medium fineness; if it is too fine or too coarse, the bars readily crumble after compression.

3. *Consolidation of the Compressed Bars.*—The bar, as it leaves the hydraulic press, is very fragile, and will break if laid on an uneven surface. It is given the desired firmness by heating for about one hour in a current of hydrogen in a tubular furnace, the temperature being slowly increased to full redness. The temperature is then very slowly raised to slightly above  $1,000^{\circ}\text{C}$ .

4. *The Burning of the Bars.*—The burning process is intended to create an intimate union between the minute crystals of tungsten, of which the bar is now composed. The operation must be carried out slowly and cautiously, as the quality of the filaments depends largely upon the success of this operation. The bars are heated to a temperature of about  $2,850^{\circ}\text{C}$ . (near the melting point of tungsten) in a special furnace shown in Fig. 35.

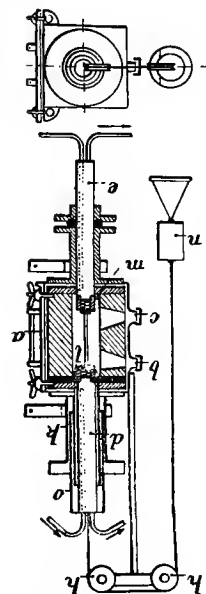


FIG. 35.—Electric Furnace.

The casing of the furnace, which is of cast iron coated inside with graphite, is provided with small tubes, *l* and *m*, for the admission and discharge of hydrogen. The wall, *u*, of the furnace is removable, and is normally attached with screws and wing nuts. The opposite wall has two windows, *b* and *c*, which permit the operation to be watched. The copper electrodes, *d* and *e*, are water cooled, the lower one being fixed whilst the upper one is suspended by a counterpoise and carries a bell, *u*, which is immersed in a cylinder, *k*, filled with mercury. The bar to be treated is attached to the electrodes by spring grips, the furnace closed, filled with hydrogen and, as soon as all oxygen is removed, the heating current is turned on. The contraction of the bar during this heating amounts to about 14 per cent. In order to obtain a temperature of  $2,650^{\circ}\text{C}$ . a current of about 53 amperes per square millimetre is required for bars having a cross-sectional area of 16 to 20 sq. mm., whilst 57 amperes are required for a temperature of  $2,730^{\circ}\text{C}$ . with bars of similar size.

5. *Working the Bars by Hammering and Rolling.*—The sintered bars, as obtained by the last process, are still brittle enough to break if dropped from a height of 30 to 40 cm., and now require to be worked at a temperature of  $1,200^{\circ}$  to  $1,300^{\circ}\text{C}$ ., but as they oxidise very rapidly in air at this temperature, it is necessary to carry out the hammering or rolling, as far as it is possible, in a current of hydrogen. The machine used for this purpose is illustrated in Figs. 36, 37, and 38.

The dies *b* have on their interior surface a tapering groove of the same size as the bar; they are mounted with the hammer *c* in a recess in the hollow shaft *a*. The hammers, which have rounded external ends, are carried by the rotation of the shaft in front of the rollers *r*, which are arranged in a ring. The rapid revolution of the shaft causes the hammers to be driven outwards by centrifugal force, but they are thrown inwards as they come into contact with each roller and transmit the blows to the dies. When the shaft is rotating at about 400 revs. per minute, the hammers give

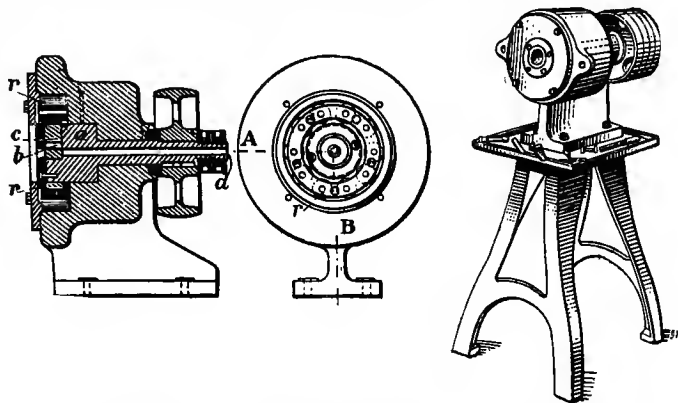


FIG. 36.—Section on A.B.

FIG. 37.—View with Cover Removed.

Fig. 38.—Complete Machine.

about 4,000 blows per minute, and these are distributed regularly over the surface of the bar. The latter, after being heated to  $1,300^{\circ}$  C. in an atmosphere of hydrogen, is quickly thrust into the machine, whilst a continuous supply of hydrogen is led in at *d* in order to prevent oxidation of the metal during the hammering. The diameter of the bar can be reduced about 4 per cent. at each treatment in the machine, so that in order to obtain a wire 1 mm. in diameter from a bar 6 mm. square about fifty treatments are necessary. Every third time that the bar passes through the machine the dies are replaced by others having a smaller diameter. When the wire has been reduced to a diameter of 0.75 mm. the metal has become so ductile that it can be bent and worked at ordinary temperatures.

#### 6. Drawing the Bars into Wire.—

Although the drawing might be performed at ordinary temperatures, the operation is considerably facilitated by heating the drawplate, the arrangement used being shown in Fig. 39.

The drawplate *a* consists of a cylindrical block in which the diamond is fixed in the usual way. Lighting gas is brought by the pipe *c* to a burner, *e*, which is arranged so as to direct its flames upon the periphery of the plate. Before entering the die, the wire passes through a cylindrical tube, which is also heated. The draw tongs *b* are similar to those usually employed in the drawing of steel wire.

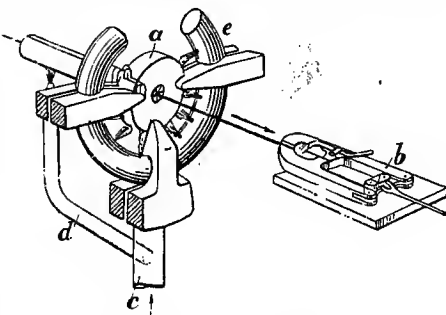


FIG. 39.—Heated Drawplate.

The drawplate is lubricated with a mixture of deflocculated graphite and water. In order to point the ends of the wires, so as to enable them to enter the die, they are either plunged into melted potassium nitrate or, if they are already thin, they are immersed in a solution of potassium cyanide and made the anodes of an electric circuit. The successive dies employed differ very little in diameter, thus, starting with a wire, 0.65 mm. diameter, they decrease by about 0.0125 mm. as far as 0.35 mm., and from this size to 0.1 mm. the interval is 0.0065 mm. From 0.1 to 0.075 mm. it is 0.03 mm. From 0.075 to 0.0375 mm. it is 0.0025 mm., and finally from 0.0375 to 0.025 mm., and below it becomes 0.00125 mm. Thus about 100 dies are necessary. During the reducing of the wire from 0.65 to 0.45 mm. the temperature is maintained at  $600^{\circ}$  to  $650^{\circ}$  C., whilst from 0.45 to 0.25 mm. it

is  $500^{\circ}$  C., whilst for smaller diameters, a temperature of about  $400^{\circ}$  C. is used. The wire thus obtained is coloured blue-black by graphite and a small amount of oxide, and is cleaned by being electrically heated to a dull red whilst passing it through a glass tube containing hydrogen.

According to English Patent, 21,513 of 1906, the tungsten wire, during the drawing operations, may be protected from oxidation by having a coating of some ductile metal such as gold, silver, or copper deposited on it.

At the present time, numerous firms are making lamps having filaments of drawn tungsten, made under licence from the patentees. As would be expected, the drawn tungsten filament has proved considerably stronger in use than those made by squirting a paste consisting of a tungsten powder and a binder, and they have also the advantage of simplifying the manufacture of the lamp, as no joining of short lengths of filament is necessary.

With pure tungsten filaments, no matter by what process they are made, a very serious defect often manifests itself after they have been in use for a short time. This defect is crystallisation, which is the result of the tungsten reverting to its original hard, brittle condition, and shows itself by irregular thickenings of the filament.

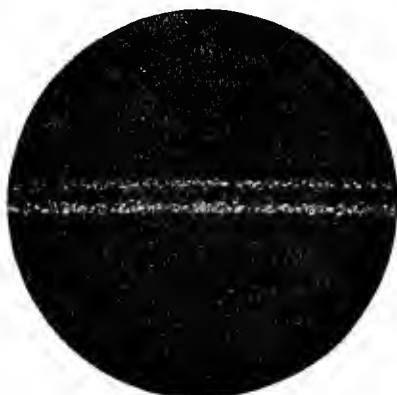


FIG. 40.—Squirted Tungsten-Thorium Filament after 1,000 Hours on Alternating Current.

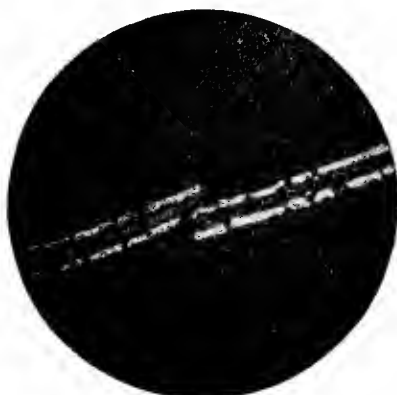


FIG. 41.—Squirted Tungsten Filament after 1,000 Hours on Alternating Current.

According to A. Lederer (*Elec. Journ.*, 1913, **10**, 1175), these thickenings occur in a longitudinal direction when a direct current is used, but if an alternating current is employed, a sort of sliding motion occurs between adjacent portions of the filament, which eventually results in fracture. Crystallisation of the filament and subsequent volatilisation is also stated to be one of the most important causes of the blackening of the bulb, which often occurs after the lamp has been in use for some little time.

These defects can be obviated, to a large extent, by using, in place of tungsten, an alloy of this metal with certain of the rare earth metals (see below).

**Tungsten Alloy Filaments.**—Numerous processes have been patented in which alloys of tungsten have been suggested for use at some stage in the manufacture of the filaments.

The processes may be roughly divided into two classes :—

1. Those in which the finished filament consists of tungsten alloyed with some other metal.
2. Those in which an alloy of tungsten is produced at a certain stage in the manufacture, but the finished filament consists only of pure tungsten.

At the present time, the only process belonging to the first group which calls for notice is that in which an alloy of tungsten and thorium is used. The process, which is covered by Austrian Patent, No. 41,247 of 1906, consists in producing

a filament composed of tungsten alloyed with thorium and other rare earth metals. The filament, thus produced, is stated to be very ductile, even in the cold, and to remain in this condition after being in use for a considerable time.

Micro-photographs of two types of tungsten filaments are shown in Figs. 40 and 41, and illustrate the difference in the appearance of the ordinary squirted tungsten filaments and those of tungsten-thorium alloy after both have been used for a considerable time.

In this country, the process is being worked by the Brimsdown Lamp Company, who make the filament by mixing colloidal tungsten (see p. 81) with certain percentages of thorium and other rare earth metals. The thorium must be in such a condition as not to promote crystallisation of the colloidal tungsten.

Several modifications of the thorium-tungsten alloy process have been patented.

Thus, according to French Patent. 447,584, finely divided metallic tungsten is mixed with about 7 per cent. of thorium tungstate and an organic binding material and filaments are made by the usual squirting process. These are reduced at a temperature near the melting point of thorium. According to English Patents, 5,026, and 8,758 of 1912, tungstic oxide is mixed with 1 to 4 per cent. of thorium and compressed into rods, which are then reduced in hydrogen at a low red heat.

**Thorium** and other rare earth metals can be obtained in a **colloidal condition** by the process which has been described by Dr Kuzel. The metal, in an extremely finely divided condition, is treated alternately with dilute solutions of certain acid and neutral reagents.

Thus, 10 kilos of the metal are heated for twenty-four to forty-eight hours with 75 kilos of 15 per cent. hydrochloric acid, well agitated, decanted, washed with distilled water, until some colloidal metal begins to pass into the filtrate. The material is next treated for about twenty-four hours with 75 kilos of a 1 per cent. solution of potassium cyanide, washed with distilled water, and heated with 75 kilos of a 1 per cent. solution of ferrous sulphate. After well washing to remove iron salts, the residue is treated with a solution of a basic substance, such as a 2 per cent. alcoholic solution of monomethylamine or a 0.5 per cent. solution of sodium hydroxide. After repeating the process several times, the metal will pass almost completely into solution in distilled water.

Processes for obtaining **colloidal tungsten** are described by Müller, *Zeits. Chem. Ind. Kolloide*, 1911, 8, 93, and also by Wohler and Engels, *Zeits. Elektrochem*, 1910, 16, 693.

The **second type of alloy process** is one in which the tungsten is alloyed with another metal in order to facilitate drawing, but the finished filament consists only of tungsten. A process of this class was successfully employed for some time by Messrs Siemens Bros. of London.

Nickel tungstate is mixed with tungstic acid, or similar plastic tungsten compound, in such proportion that the alloy produced on heating to 1,650° C. in hydrogen contains about 12 per cent. of nickel. (At a later date this quantity was reduced to 2 per cent.) The alloy, thus produced, is stated to be very ductile, and may be drawn into wire or rolled. After making the alloy into filaments by drawing, the nickel is expelled by heating *in vacuo*. This process has now been discontinued, as considerable blackening of the bulb took place after the lamps had been in use for some time.

Another method of producing this alloy was to mix the finely divided metals in the correct proportions, compress in rods, and heat these at the melting point of nickel in an atmosphere of hydrogen.

A machine suitable for making filaments from plastic material, such as tungsten powder mixed with a binder or the colloidal metal, is described in English Patent, 11,252 of 1912.

The machine comprises a rotating horizontal disc, having projecting studs on its outer edge. These studs intersect a filament as it leaves a fixed squirting orifice, so that the filament forms loops hanging down between the studs. These loops are carried round by the disc until they come opposite to a pair of burners which heat the two branches of the loop simultaneously at points near the studs, so as to sever the loop from the continuous filament. At this instant a rod is thrown forward beneath the loop so as to invert it as it drops, and guide it on to its support. This support may be a conductor, and can be heated so that the loops hanging on it will take its shape. The studs pass a brush before they again reach the squirting nozzle, so that the short pieces of filament remaining on them are removed.

It is very essential that all the small loops which go to make up a discontinuous filament, *i.e.*, one which is not made from one piece of wire, should be of the same cross-sectional area and resistance, otherwise the life of the lamp will suffer. In some works it is customary to actually weigh each section of filament on an extremely sensitive balance. In the case of a lamp having a filament of drawn wire, it is very essential that this should be of uniform diameter.

As many of the details in connection with the finishing and mounting of the metallic filaments are trade secrets they cannot be given here, but the following is a brief general account of certain portions of the process.

The central "**spider**" upon which the filament is to be wound is produced by moulding a glass rod to the desired shape, and then fixing the supporting metal hooks by hand. It is usual to make the upper and lower series of hooks of different metals, that used for the upper series being selected for its rigidity, whilst a more elastic material is used for the lower series. A very frequent arrangement is to make the upper row of fairly stout nickel wire, whilst the lower supports are made of molybdenum or an alloy of nickel with tungsten or molybdenum. This arrangement gives a fairly wide range of elasticity, and thus allows for the expansion and contraction of the filament which occurs in use. In some cases the necessary elasticity is attained by the use of thin copper wire coiled in helical form in place of the lower series of hooks. The actual shapes of the hooks used exhibit wide variations; thus, if continuous filaments are used, the support consists of a straight wire with a small terminal hook or loop; but if a discontinuous filament be employed, the individual loops require to be separately fixed to the wires of the "spider," and this has to be done either by using a tungsten solder or by employing a "pinched" joint.

The filament is usually wound very loosely on to the "spider," in order to allow for the permanent contraction which occurs when a current is passed through the wire; and a current is then sent through it for a few seconds in order to test the work.

The connection between the leading-in wires and the metal filament is made in three sections, as mentioned under carbon filament lamps (see p. 74).

The filament and spider is sealed into the bulb in the usual manner, but in order to remove from the latter all traces of moisture, which is stated to be one of the causes of blackening, a small quantity of some phosphorus compound is painted upon the stem. For this purpose a solution of red phosphorus in alcohol and ether is often employed. Owing to the high temperature employed in the final evacuation, the phosphorus is completely volatilised. The removal of the air from metallic filament lamps requires to be more thoroughly carried out than is necessary in the case of those having carbon filaments, and is usually performed by means of one of the modern types of pump mentioned on p. 75.

In some works it is customary to perform the final evacuation of the lamps at a temperature of 200° to 300° C. The evacuated lamp is affixed to its metal socket, and tested in the same way as has been described already for the carbon filament lamp (see p. 75).

The last three stages in the manufacture of a metal filament lamp are shown in Fig. 42, B, C, and D).

**Nitrogen-filled Lamps.**—During the past two years an interesting development has taken place in the manufacture of high efficiency electrical illuminants, by the introduction of a glow lamp having a tungsten filament not enclosed in an evacuated globe, but in one which contains a quantity of an inert gas, the pressure of which at working temperatures is about equal to that of the atmosphere.

The invention appears to have been at first announced in a paper by I. Langmuir and J. A. Orange (*Proc. Amer. Inst. Elec. Eng.*, 1913, p. 1915). These workers, whilst investigating the causes of the blackening of metallic filament lamps, found that this defect, which is largely due to volatilisation of the filament, was considerably minimised by introducing an inert gas into the bulb. The gas found to be most suitable was nitrogen, as the loss of heat by convection

was considerably less than when hydrogen was used. It was also found that the loss of efficiency of a tungsten filament in an atmosphere of an inert gas near atmospheric pressure was greater for wires of small diameter (0.002 in.) than for larger wires (over 0.005 in.), hence the finer wires require to be coiled into a tightly wound helix, or otherwise concentrated into a small space. A filament wound in such a manner and mounted on its "spider" is shown in A, Fig. 42. It may be here mentioned that the helical filament is also coming into use for the evacuated type of lamp when required to give most of its light in the horizontal plane.

It was found that lamps made in this manner had an efficiency much greater than those of the usual evacuated type. Nitrogen-filled lamps are now being produced by several makers, and may be roughly classified into—(1) Large unit lamps consuming 0.4 to 0.5 watt per candle power, and having a life of at least 1,500 hours. These lamps take a current of 20 to 30 amperes, and hence must be run on a low voltage circuit. (2) Small unit lamps taking currents of about ten amperes at voltages as low as 4 or 5. Their specific power consumption with

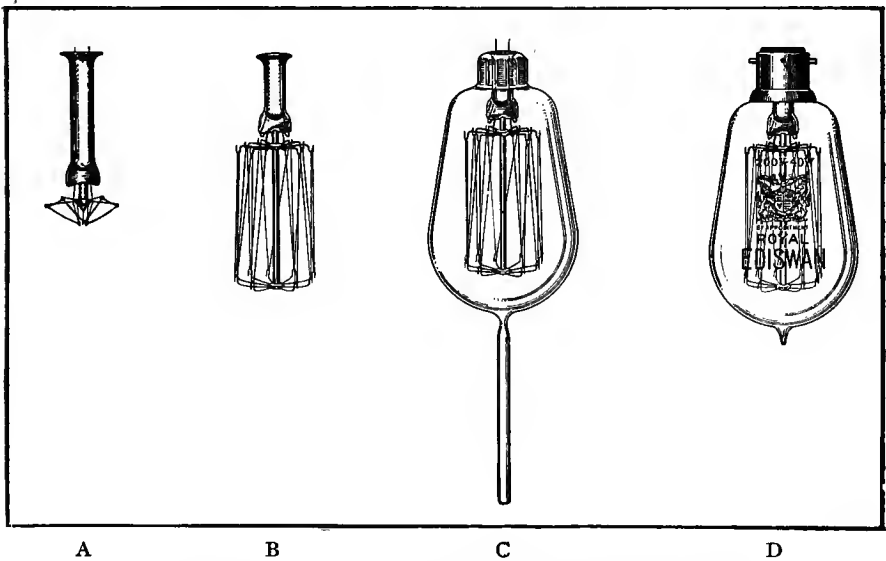


FIG. 42.—Stages in the Manufacture of a Metallic Filament Lamp.

a life of 1,000 hours varies from 0.6 to 1.0 watt per candle power. (3) Large unit lamps of several thousand candle power, run on standard lighting circuits of 110 volts, consuming 0.5 watt or less, per candle power. The maximum efficiency, at present, can only be attained with lamps taking large currents. The light given by the nitrogen-filled tungsten lamp is of a very penetrating character, and more adapted for replacing arc lighting than for the illumination of small interiors. A description of the "Nitra" lamp, one of the best known of this class, is given in *Helios*, 1913, 19, 316.

A method for the analysis of metallic filaments, which permits of individual filaments being examined, has been described by C. Baskerville (*Trans. New York Electrical Soc.*, 1912, No. 1).

**Cost of Production of Metal Filament Lamps.**—The profits on the manufacture of metal filament glow lamps are stated to be very small at the present time. The following figures, which are actual works costs, and show the outlay required for material and labour for the production of the individual parts of the lamps and the finished article, are from an account by H. T. Erb (*Electrical Review*, 1913, 73, 938).

The lamp under consideration is a 220 volt, 25 watt, metal filament.

TABLE XXI.  
COST PER 1,000 LAMPS

	Materials.	Wages.	Breakages.
	Shillings.	Shillings.	Shillings.
Bulb	37.1	4.5	0.63
Crown -	4.9	1.52	0.32
Electrodes	28.0	2.25	0.29
Stem	41.3	7.2	0.49
Star	26.3	13.15	..
Attachment	133.0	32.10	5.04
Melting-on	37.1	9.7	15.85
Pumping	...	11.8	18.7
Flashing	0.6	1.96	4.70
Adjustment and completion	21.8	9.35	6.90
	261.0	85.0	53.0

In the above table no allowance is made for the cost of gas, electric current, standing charges, and unproductive labour.

**The Efficiency of Metallic Filament Lamps.**—It is frequently stated that the drawn wire tungsten filament lamp has an efficiency of 1 watt per English candle power, with an average useful life of at least 1,000 hours. But according to statements by the makers, it would appear that this efficiency is rarely reached under ordinary conditions of working, especially in the case of the smaller candle power lamps. An average figure would appear to be between 1.1 and 1.25 watts per candle power. The useful life of an electric glow lamp is defined as the time taken for the mean horizontal candle power of the lamp to decrease 20 per cent. from its standard value, when run under standard conditions.

The characteristics of the various types of incandescent electric glow lamps are shown in the following table:—

TABLE XXII.

Material.	Watts per Hefner Candle Power.	Hefner Candle Power per Sq. Mm. of Surface.	Temperature of Incandescence.	Ratio of Hot to Cold Resistance.
Carbon	3.5	0.154	1,800° C.	0.5
Osmium	1.5	0.331	1,900° C.	8.94
Tantalum -	1.6	0.307	1,700° C.	6.07
Tungsten -	1.15	0.441	2,150° C.	12.12

The use of numerous other metals as metallic filaments has been patented. Thus, Kellner, in addition to tungsten, suggested thorium, titanium, and chromium (English Patent, 19,785 of 1898), whilst the use of metallic vanadium or niobium is covered by English Patents, 12,156, 12,157, and 12,159 of 1902. Carbides of certain metals have also been suggested, such as vanadium carbide (English Patent, 19,264 of 1905), cerium carbide, titanium carbide (see p. 42), and zirconium carbide (see p. 50). Cerium nitride is mentioned in English Patent, 929 of 1906. Numerous attempts have been made to utilise silicon as a filament. In one of these (French Patents, 446,140 and 446,310 of 1912) carborundum is used as the starting point. The use of metallic uranium is mentioned in United States Patent, 1,106,384 of 1914, and cobalt in French Patent, 460,093 of 1913.

### PATENT LITERATURE

A large number of patents dealing with the manufacture of incandescent electric lamps have been granted in many countries during the past few years, and it is not possible to give a complete list of these here.



During 1913, it was announced by the General Electric Company, the British Thomson-Houston Company, and Siemens Bros. Dynamo Works, all of London, that they had arranged to licence each other to operate all patents which they then held individually. The principal of these patents are stated to be as follows:—

English Patents, Nos. 27,712 of 1903; 20,277, 23,899, 27,713, 27,714 of 1904; 19,379, 20,175, 23,437 of 1905; 3,213, 6,803, 12,325, 21,513, 23,335, 18,622 of 1906; 3,174, 8,563, 16,503, 16,530, 16,531 of 1907; 5,387, 8,421, 17,350, 19,932 of 1908; 23,499 of 1909; 2,759, 8,031, 15,621, 23,121, 24,549 of 1910; 1,161, 1,162, 8,004, 17,722, 20,224, 20,380, 27,360, 28,576 of 1911; 873, 874, 2,284, 3,840, 11,439 of 1912.

It is understood that a large number of the other makers in the United Kingdom are also working these patents under licence.

**Acknowledgments.**—Thanks are due to the **Edison & Swan United Electric Light Company** of Ponders End, **Messrs Siemens Bros.** of Dalston, London, N.E., and the **Brimsdown Lamp Company** of Brimsdown, Middlesex, for information concerning the method of manufacture of incandescent electric lamps, and to the first-mentioned company also for the loan of certain of the blocks illustrating this chapter.



## CHAPTER VII



### Uranium



## CHAPTER VII

# URANIUM

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ALTHOUGH uranium cannot be classed amongst the rare earths, its intimate association, in the mineral form, with radium renders a brief account of its occurrence and properties desirable. More important still, perhaps, is the fact that the uranium content of an ore is often a fairly accurate measure of the quantity of radium present. Besides radium, most uranium ores carry other radioactive matter, such as actinium, polonium, and ionium.

### Natural Occurrence

Uranium oxide was first isolated by Klaproth in the year 1789 from the mineral, **pitchblende**. The metal itself was first obtained by Péligré in 1842. Combined with other elements, uranium has been found in a large number of minerals; the majority of these, however, are of somewhat infrequent occurrence. A fairly complete list of these minerals is given in *U.S. Bur. Mines, Bull.* 70, p. 92. Amongst the more important uranium minerals may be mentioned **pitchblende** or **uraninite**, **carnotite**, and **autunite**. The less frequent minerals, **thorite** and **thorianite**, have already been described under thorium (see p. 8).

Small quantities of uranium oxide are found in most of the minerals which contain phosphates and silicates of the rare earths, *e.g.*, **xenotime**, **columbite**, **cerite**, and **monazite**.

**Pitchblende**, which was for some years the most important uranium mineral, consists essentially of uranium oxide, together with varying amounts of rare earths, lead, lime, bismuth, etc. The mineral is sometimes found in octahedral crystals, but more commonly occurs massive. It varies in colour from greyish to dark green, brown, and black, having a conchoidal fracture, and a submetallic lustre. The specific gravity varies from 6.4 to 9.7, and the hardness is usually about 5.5. **Clevite** and **bröggerite** are the names applied to certain varieties of pitchblende rich in the rare earths.

**Carnotite**.—This promises to become in the future the largest source of uranium, and consequently of radium. Chemically, the mineral is a vanadate of uranium and potassium, sometimes containing small quantities of calcium, barium, and iron. The mineral usually occurs in the form of very minute crystals, of a canary yellow colour, as incrustations on certain other minerals. This mineral is also valuable for its vanadium content.

**Autunite.**—Anhydrous phosphate of calcium and uranium, with the formula  $\text{Ca}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ . It is a bright yellow mineral, often crystallising in orthorhombic plates, having a specific gravity of 3.5 to 3.9. It is sometimes termed uranium mica.

### Geographical Distribution of Uranium Ores

The most celebrated deposits of **Pitchblende** occur in Austria, at Joachimsthal, where the mines have been worked since 1517 for various minerals, including silver and bismuth. It is only during the last ten years, however, that they have been extensively worked for uranium. At the present time, the mines are worked by the Austrian Government for uranium and radium, the export of the latter substance from Austria being prohibited. An account of these deposits is given by R. Beck (see above). In Saxony, the mineral occurs at Johanngeorgenstadt, Marienburg, Freiburg, and Schneeberg, and also at Příbram, in Bohemia.

In **Cornwall**, pitchblende has been found in many mines of the tin area, associated with nickel and cobalt (as at Joachimsthal). An account of these mines is given in "The Geology of Falmouth and Truro, and of the Mining Districts of Camborne and Redruth," and "The Geology of the Country around Bodmin and St Austell," both of these publications being issued in the Memoirs of the Geological Survey of England and Wales. In the **United States**, pitchblende occurs in many localities in Gilpin County, Colorado, and has been mined to some extent. An account of recent work at these mines is given in *U.S. Bureau of Mines, Bull.* 70. The mineral in a very pure form has been found in **German East Africa**, but it would appear that the quantity available is small (see also W. Marckwald, *Centralbl. Min.*, 1906, 761). It also occurs in the Porcupine district of Ontario, **Canada**, where it is stated to contain a larger proportion of radium than the Austrian mineral. In **India**, the mineral occurs at the Singar mica mines of the Gaya district, and is now being worked. For an account of this deposit see *Records of Geol. Sur. India*, 1914, 44, 20.

Uranium ores have been exported from the **United States** for a number of years past, but it would appear that it was not until about the year 1912 that the authorities realised how much radium was leaving the country in this form. Carnotite ores occur chiefly in Colorado and Utah in the area lying between the Rocky Mountains of Colorado and the San Rafael Swell of Utah, the Denver and Rio Grande railroad, and the Arizona and New Mexico line. In this area the chief deposits of Colorado occur in the vicinity of Paradox Valley, M'Intire Canon, Mesa Creek, and Gateway; whilst those of Utah include the La Sal Mountains, Dry Valley, Yellow Cat Wash, San Rafael Swell, and the Henry Mountains (F. L. Hess, *Econ. Geol.*, 1914, 9, 676). An investigation, carried out by R. B. Moore and K. L. Kithil (*U.S. Bur. Mines, Bull.* 70) showed that the richest deposits are those of the Paradox Valley. Much uranium ore is wasted in the process of sorting to get a marketable grade, owing to the lack of a cheap and efficient method of concentrating the ore.

Considerable attention has been directed, during the past few years, to the economic possibilities of the **South Australian** deposits of uranium ore. So far, deposits have been worked in two localities, *i.e.*, Radium Hill, 20 miles E.S.E. of Olary station on the Petersberg-Brokenhill railroad, and between Mts. Painter and Pitt in Flinders Camp, about 80 miles east of Farina. In the Olary district, where the work has so far proved the more successful, the uranium occurs, in the form of carnotite, as an incrustation on titaniferous magnetite. The ore, which has been worked for over two years, is magnetically concentrated at the mine, so that each ton of concentrate will give about 3.6 mg. of radium. The concentrates are treated at Woolwich, near Sydney. The Mt. Painter deposits, which yield autunite, carnotite, uranophane, and torbernite, appear to be rather less successful than those of Olary. For an account of recent progress in these localities see L. K. Ward, "Review of Mining Operations in South Australia," No. 19, p. 26, and *Min. Journ.*, 1913, 103, 1134.

During the past few years, **Portugal** has produced a quantity of uranium ore; chiefly autunite, torbernite, and small quantities of urano-circite (a hydrous phosphate of barium and uranium). The richest deposits are stated to occur in the district of Guarda, in the province of Beira, and to be closely connected with occurrences of tin and tungsten. The ore mined is stated to have an average content of about 1 per cent. of uranium oxide ( $\text{UO}_3$ ). The deposits are being worked by several companies, one of which employs about six hundred men.

Deposits of carnotite have been found in several localities in **Russia**, the largest being probably that of Tjua-Mujun in the Andijan district of Central Asiatic Russia. These and other Russian deposits have been described by E. de Hautpicks in "Radioactive Minerals of Russia" (*Min. Journ.*, 1911, 92, 185), and F. L. Hess (*Min. Res. U.S.*, 1912, pt. i., 1031).

In **Madagascar**, autunite, blomstrandite, euxenite, and fergusonite occur in pegmatites, but the quantity available commercially is probably small.

In **Sweden**, a carbonaceous substance found in Silurian limestone and known as "Kulm" contains a small percentage of uranium, and it is proposed to burn it and recover the uranium from the ash. The "Kulm," on burning, gives from 15 to 56 per cent. of ash, which contains 1 to 3 per cent. of uranium oxide.

**Commercial Value of Uranium Ores.**—The value of uranium ore is almost entirely dependent upon its radium content. At the present time, ores carrying less than 2 per cent. of uranium oxide ( $U_3O_8$ ) cannot be readily sold in this country. The price obtainable is now (Oct. 1914) about £30 per ton for ore containing 2 per cent. of uranium oxide ( $U_3O_8$ ). Sometimes an allowance is also made for any vanadium in the ore.

### Production of Uranium Ore

The following table shows the production and value of uranium ore so far as statistics are available :—

TABLE XXIII.

	1910.		1911.		1912.	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
	Metric Tons.	£	Metric Tons.	£	Metric Tons.	£
United Kingdom -	77	...	68	...	43	...
Austria	6,522	4,039	5,785	3,522	10,894	6,472
Germany *	95	11,000	82	8,250	5,053	3,200
Indo-China -	1.1	390	1.9	200	...	...
Madagascar	2	30	29	349	1	..
Portugal	138	3,776	4,409	5,737	...	1,310
United States †	No returns.	...	25	62,731	26	102,669

**Composition of Uranium Ores.**—The chemical composition of certain ores of uranium is shown in the following table :—

TABLE XXIV.

	Formula.	1. Pitchblende. Johanngeorgenstadt.	2. Carnotite. S. Australia.	3. Autunite. Autun.	4. Torbernite. Cornwall.
Uranic oxide	$UO_3$	59.30 }	47.8	61.34	61.00
Uranous oxide	$UO_2$	22.33 }			
Vanadic oxide	$V_2O_5$	...	16.8	...	...
Ferric oxide	$Fe_2O_3$	0.21	19.4	...	...
Alumina	$Al_2O_3$	0.20	5.7	...	...
Manganous oxide	$MnO$	0.09	...	...	...
Lime	$CaO$	1.00	1.0	5.24	0.62
Magnesia	$MgO$	0.17	...	...	...
Lead oxide -	$PbO$	6.39	1.3	...	...
Copper oxide	$CuO$	...	...	...	8.56
Potash -	$K_2O$	...	5.2	...	...
Soda	$Na_2O$	0.31	1.8	...	...
Phosphoric acid	$P_2O_5$	0.06	trace	14.97	13.94
Arsenic oxide	$As_2O_5$	...	...	...	1.96
Silica	$SiO_2$	0.50	...	...	...
Water	$H_2O$	3.17	...	19.66	14.16

1. Analysis by W. F. Hillebrand, *Amer. Journ. Sci.*, 1891, 42, 390. 2. G. S. Blake, *Min. Mag.*, 1910, 15, 271. 3. A. H. Church, *Journ. Chem. Soc.*, 1875, 28, 109. 4. Church, *Chem. News*, 1865, 12, 183.

**Chemical Treatment of Uranium Minerals.**—For the production of uranium compounds from pitchblende, the ore is first roasted in order to remove most of the sulphur, arsenic, and molybdenum, and is then heated in a reverberatory

\* Returns are for uranium and tungsten ore.

† Values are for uranium and titanium ores, the quantities being calculated to the equivalent amount of  $U_3O_8$ . The quantities of "uranium and vanadium ore" produced in 1911, 1912, and 1913 were 8,468, 18,000, and 27,900 tons respectively.

furnace with sodium carbonate to which a little sodium nitrate has been added. The fused mass is washed with water, extracted with dilute sulphuric acid, and filtered, the insoluble residue being used for the production of radium. To the filtrate containing the uranium, excess of sodium carbonate is added, thus causing basic carbonates of iron, aluminium, nickel, and cobalt to be precipitated. After filtration, the uranium in solution is precipitated either by adding sodium hydroxide or by vigorously boiling the solution after neutralising it with dilute sulphuric acid. The sodium diuranate thus obtained is pressed, dried, and ground. The commercial salt has the composition  $\text{Na}_2\text{U}_2\text{O}_7 \cdot 6\text{H}_2\text{O}$ .

If the black oxide,  $\text{U}_3\text{O}_8$ , is required Wohler's method may be used. In this, the solution in dilute sulphuric acid is treated with sulphuretted hydrogen to remove arsenic, antimony, copper, lead, and bismuth, filtered, and after oxidising the filtrate with nitric acid, excess of ammonia is added. The precipitate, which consists of hydroxide of iron and ammonium uranate, is digested with a concentrated solution of ammonium carbonate containing excess of ammonia, in order to dissolve the ammonium uranate. After filtering the liquid and allowing it to cool, ammonium uranyl carbonate crystallises out. A further quantity of ammonium uranate can be obtained from the mother liquor by adding ammonium sulphide to precipitate the zinc, nickel, or cobalt, and evaporating the filtrate. Both ammonium uranate and ammonium uranyl carbonate give  $\text{U}_3\text{O}_8$  on ignition.

The possibility of utilising phosphatic uranium micaceous minerals, such as autunite and copper autunite, as sources of radium and uranium, is discussed by F. Glaser (*Chem. Zeit.*, 1912, **36**, 1166). It is stated that although the processes of extraction are comparatively simple, the profitable working of autunite is only possible when the percentage of uranium is high.

**Metallic uranium** can be prepared by several methods, one of which consists in mixing five hundred parts of  $\text{U}_3\text{O}_8$  with forty parts of sugar charcoal and reducing the mixture in a carbon tube in the electric furnace. The crude product, thus obtained, which still contains some carbon, is purified by being heated in a crucible, brasqued with  $\text{U}_3\text{O}_8$ , which is embedded in another crucible brasqued with titanium. The effect of this latter is to prevent access of nitrogen to the reduced uranium (H. Moissan, *Comptes rend.*, 1893, **116**, 347). The metal may also be prepared by the electrolysis of the fused double chloride of uranium and sodium in an inert atmosphere using carbon electrodes (H. Moissan, *Comptes rend.*, 1896, **122**, 1088).

For the production of **ferro-uranium**, reduction with aluminium is stated to be unsuitable, as the final product then contains aluminium, corundum, and uranium oxide (F. Giolitti and G. Tavanti, *Gaz. Chim. Ital.*, 1908, **38**, 239). It is stated, however, that Stavenhagen's modification of the "thermit" process can be used (A. Stavenhagen and E. Schuchard, *Ber.*, 1902, **35**, 909).

### Utilisation of Uranium and its Salts

So far, very few uses demanding much material have been found for **metallic uranium**. For a short time an impure form, containing some carbide, was employed as the sparking medium for automatic cigar lighters, but the material has now been superseded by the more efficient cerium-iron alloy (see p. 28). Metallic uranium has been suggested for use in electrodes of arc lamps. When enclosed in a quartz globe surrounded by an inert atmosphere, the arc between such electrodes gives a light very rich in ultra-violet rays. (See French Patent, 418,280, 15th July 1910.) According to the third and fourth additions to the above patent, a vacuum is substituted for the inert atmosphere, and in the seventh addition, dated 26th May 1911, a special type of lamp with mercury cathode is described and is stated to be suitable for sterilising liquids by means of ultra-violet rays.

Various attempts have been made to utilise **ferro-uranium** in the manufacture of special steel. In general, it may be stated that uranium steel has properties very similar to those of tungsten steel, but as ferro-tungsten can be produced at a



lower price than ferro-uranium, not much progress has been made in the use of the latter alloy in steel manufacture.

Uranium salts have long been known as **colouring agents for glass**. The colour produced is an opalescent yellow which is green by reflected light. Owing to the fact that about 20 per cent. of uranium oxide has to be used to produce the colour, the glass is somewhat expensive.

**In the Ceramic Industry** uranium salts find a limited use for the production of yellow and orange glazes, the salts most employed being the "yellow oxide" (sodium diuranate) and the green oxide ( $U_3O_8$ ).

The colouring power of uranium is strong, 0.006 equivalent giving a good colour, the depth of which is stated to be largely dependent upon the amount of lead present in the glaze. By suitable adjustment of the composition of the glaze and the conditions of firing, uranium can be made to give colours varying from yellow and orange to brown and dark olive-green. An account of the use of uranium salts in glazes is given by F. H. Riddle, *Trans. Amer. Ceram. Soc.*, 1906, 8, 210, and by L. H. Minton, *Trans. Amer. Ceram. Soc.*, 1907, 9, 771.

Uranium salts have been suggested for use as **mordants** for silk and wool, but no great progress seems to have been made in this direction. (See also E. Odenheimer, *Farber Zeit.*, 1894, 5, 17.)

Uranium oxide has been utilised as a catalyst in the synthesis of ammonia from nitrogen and hydrogen (Haber and Le Rossignol, *Zeits. Elektrochem.*, 1913, 19, 53).

Uranium salts have been used to a very limited extent for producing brown colours on textile fibres by treating them first with uranium nitrate solution and then with solutions of either ferrocyanide of potassium, gallic acid, tannic acid, or pyrogallol. (See P. Werner, *Bull. Soc. Ind. Mulhouse*, 1892, 542, and E. Odenheimer, *loc. cit.*)

In photography, uranium nitrate has been suggested as a sensitising agent for paper (C. T. Roche, *Journ. Soc. Chem. Ind.*, 1888, 7, 231), and according to English Patent, 10,072 of 12th May 1896, uranium acetate combined with a suitable acid can be used with potassium ferrocyanide for intensifying or reducing negatives. With potassium sulphocyanide it can be used for toning bromide prints.

**Analysis of Uranium Minerals.**—The mode of attacking uranium minerals varies largely with their nature. Thus, carnotite and autunite can be readily dissolved with the aid of dilute nitric acid, whilst thorianite and pitchblende are attacked by boiling concentrated nitric acid, but certain varieties of thorite are very difficult to dissolve, and require fusion before a satisfactory solution can be obtained. In the absence of vanadium and phosphates the following procedure may be adopted.

When the solution of the mineral is complete, the acid solution is filtered, diluted, and slowly poured into excess of ammonium carbonate. After allowing to stand for some hours, the solution is filtered, the precipitate dissolved in acid, and re-treated with ammonium carbonate. The combined filtrates will now contain all the uranium, and may also carry small quantities of rare earths and calcium. The rare earths must be removed by precipitation with ammonium oxalate (see p. 10). The filtrate from this treatment is evaporated to dryness and ignited to remove oxalates, redissolved in nitric acid, and the latter removed by repeated evaporation with sulphuric acid. The residual sulphates are dissolved in a small quantity of water, and three times their bulk of alcohol added. After being allowed to stand for twelve hours, the precipitated lime is filtered and washed with alcohol. The alcoholic filtrate is evaporated to dryness, ignited, dissolved in nitric acid, and the uranium precipitated as ammonium uranate by the addition of a slight excess of ammonia. The solution is filtered, and the precipitate, after being washed with a 4 per cent. solution of ammonium nitrate, is dried, ignited, and weighed as  $U_3O_8$ .

When phosphates are present, difficulty is often experienced in carrying out the analysis, as described above, owing to uranium phosphate being somewhat difficultly soluble in ammonium carbonate, and when calcium is present this is also precipitated with the uranium phosphate. The following process overcomes these difficulties. The uranium solution is diluted, and a solution of ferric sulphate is added in slight excess of the amount required to precipitate the phosphorus as ferric phosphate. The iron and phosphate are then precipitated together by the basic acetate method, using ammonium acetate and keeping the solution slightly acid. The solution is filtered, the precipitate washed a few times with a very dilute solution of ammonium acetate, then dissolved in hydrochloric acid, and the precipitation repeated. The combined filtrates are evaporated to dryness with hydrochloric acid, the residue treated, as already described, for the removal of rare earths and calcium and the estimation of uranium oxide.

When vanadium is also present, as in carnotite, the analysis is much more intricate, owing to the necessity of separating this constituent from the uranium. Methods used by firms dealing in these ores will be found, in detail, in *U.S. Bur. Mines, Bull.* 70.

Methods for the analysis of ferro-uranium are given by W. Trautmann, *Zeits. angew. Chem.*, 1911, 24, 61.



## CHAPTER VIII



## Vanadium



## CHAPTER VIII

# VANADIUM

### LITERATURE

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 H. MANZ.—“Die Vanadiumerze und Ihre Aufarbeitung.” *Metal und Erz*, 1913, **10**, 379.

DURING the past ten years increasing attention has been devoted to the utilisation of metallic vanadium and its salts. First, by reason of its utility in the production of special steels, and secondly on account of its being a by-product in the manufacture of radium from carnotite.

### Natural Occurrence

Minerals containing vanadium are of fairly common occurrence, being frequently found in arenaceous and other sedimentary rocks associated with other metallic minerals such as those of copper and iron. In spite of its frequent occurrence, however, ores of vanadium of sufficient richness to be of commercial value are somewhat rare.

The most commonly occurring vanadium minerals are **carnotite**, **patronite**, **roscoelite**, and **vanadinite**. Of less importance are descloizite (a basic vanadate of lead and zinc), mottramite (vanadate of lead and copper), and pucherite (bismuth vanadate). Vanadic oxide is a minor constituent of many bauxites, iron ores, and sometimes constitutes a large portion of the ash of certain lignites, coals, and bituminous substances.

**Carnotite** is a uranyl potassium vanadate and has already been described under “Uranium” (see p. 93).

**Patronite** is a greenish coloured sulphide of vanadium, which approximates in composition to the formula  $V_2S_9$ ; often occurring mixed with carbonaceous matter. It is frequently found associated with pyrites and free sulphur. When calcined, it burns readily and loses about 45 per cent. of its weight. The mineral has a hardness of 2.7 and a specific gravity of about 2.71.

**Roscoelite** is a muscovite mica in which a part of the aluminium has been replaced by vanadium. It occurs in minute mica-like scales which may vary in colour from green to brown. Its specific gravity is usually about 2.9. This is probably the most important vanadium ore produced in the United States.

**Vanadinite** is a chloro-vanadate of lead to which the formula  $9\text{PbO}, 3\text{V}_2\text{O}_5, \text{PbCl}_2$  has been assigned. It would thus contain, when pure, 19.4 per cent. of vanadic oxide ( $\text{V}_2\text{O}_5$ ). The mineral, which occurs in prismatic hexagonal crystals, has a specific gravity of 6.6 to 7.1. It may vary in colour from ruby red to yellowish or reddish brown.

**Composition of Vanadium Minerals.**—The chemical composition of typical samples of several vanadium minerals is shown in the following table:—

TABLE XXV

	Formula.	Vanadinite,* Arizona.	Roscoelite.†
		Per Cent.	Per Cent.
Vanadic oxide	$\text{V}_2\text{O}_5$	18.64	28.36
Arsenic oxide	$\text{As}_2\text{O}_5$	Trace	...
Ferric oxide	$\text{Fe}_2\text{O}_3$	0.40	1.23
Alumina	$\text{Al}_2\text{O}_3$	...	13.94
Lime	$\text{CaO}$	...	0.62
Magnesia	$\text{MgO}$	...	2.06
Copper oxide	$\text{CuO}$	0.18	...
Lead oxide	$\text{PbO}$	77.00	...
Potash	$\text{K}_2\text{O}$	...	8.87
Soda	$\text{Na}_2\text{O}$	...	0.92
Chlorine	$\text{Cl}$	2.69	...
Phosphoric acid	$\text{P}_2\text{O}_5$	0.72	...
Water	...	...	2.42

### Geographical Distribution of Vanadium Ores

Probably at least 70 per cent. of the vanadium produced commercially is obtained from the ores occurring at Minasragra, about twenty miles from Cerro de Pasco, **Peru**.

The vanadium here occurs in several mineral forms, amongst which may be mentioned a red calcium vanadate, which may carry as much as 50 per cent. of vanadic oxide ( $\text{V}_2\text{O}_5$ ) and is found in small pockets and crevices. A blue-black vanadium shale also occurs, which may carry as much as 13 per cent. of vanadic oxide and 5 per cent. of sulphur. The principal vanadium-bearing mineral, however, is patronite, which occurs in veins enclosed by porphyry dykes. An analysis of this mineral showed it to contain:—vanadium sulphide, 39.94 per cent.; molybdenum sulphide, 1.57; free sulphur, 30.57. This sample, on calcination, gave a product containing 58.08 per cent. of vanadic oxide. Descriptions of these deposits are given by D. F. Hewett, *Trans. Amer. Inst. Min. Eng.*, 1909, 40, 291, and W. F. Hillebrand, *Journ. Amer. Chem. Soc.*, 1907, 29, 1019.

An interesting deposit of asphaltic material occurs beneath these patronite beds. It is very rich in sulphur, deficient in hydrogen, and contains from 2 to 3 per cent. of vanadic oxide. Several attempts have been made to work certain of these asphaltic deposits for vanadium. Similar carbonaceous deposits occur in many localities in Peru, and also in the United States, in Oklahoma, and Nevada.

**Roscoelite** has been mined, in the **United States**, for a number of years, between Placerville and Newmire in San Miguel County, Colorado. It has been stated that these are probably the largest vanadium deposits yet located in the United States. The ore as mined carries an average of about 1.5 per cent. of vanadic oxide, but as the deposits are large and easily worked the operations can be conducted at a profit. For references to literature dealing with these and other deposits of vanadium in the United States see *U.S. Bur. Mines., Bull.* 70, p. 51.

**Vanadinite** deposits at Cutter, New Mexico, **United States**, were worked for some time, but were recently abandoned owing to difficulties encountered in the metallurgical treatment of the ore (see also F. L. Hess, *U.S. Geol. Surv., Bull.* 530, p. 157). The mineral also occurs, in the United States, in Arizona and California. In **Mexico**, it occurs at Villa Rosales, Chihuahua, Coyame, and Iturbide.

In **Spain**, important deposits of vanadinite occur and have been worked near Santa Marta, Estramaduras. The sandstone ore is stated to contain an average of 3 per cent. of vanadic oxide which is raised to about 14 per cent. by concentration. These deposits have been worked for vanadium since 1899, and up to 1906 they supplied the greater part of the world's requirements.

\* Genth, *Trans. Amer. Phil. Soc.*, 1885, 22, 365.

† Roscoe, *Proc. Roy. Soc.*, 1876, 25, 109.

In **Argentina**, deposits of descloizite occur in the River Plate district, and these have been worked to a small extent.

At one time the preparation of vanadium on a large scale was carried out near Manchester, **England**, from mottramite, which occurs, with copper ore, in the Keuper sandstone beds at Alderley Edge and Mottram St Andrews, Cheshire. It would appear, however, that the payable portion of the deposits was worked out some years ago and the mining discontinued.

Deposits containing vanadium minerals also occur at the Wanlock Head Mine of Dumfries, Scotland, and in Portugal, Sweden, Russia, and Germany.

### Production of Vanadium Ore

The available statistics of the quantity and value of vanadium ore produced during recent years are shown in the following table :—

TABLE XXVI

	1910.		1911.		1912.	
	Quantity. Metric Tons.	Value £	Quantity. Metric Tons.	Value £	Quantity. Metric Tons.	Value £
Argentina	...	...	14	...	40	...
Peru -	3,131	237,880	2,251	215,000	3,048	150,000
Spain -	...	...	199	2,860	38	730

No statistics are available regarding the quantity of vanadium ore produced in the United States as in the returns the ores are included under the heading "Uranium and Vanadium Ore."

### Extraction of Vanadium from its Ores

The method of extraction employed on a commercial scale varies largely with the nature and richness of the ore. Usually, the difficulties encountered lie not so much in obtaining the mineral in solution as in the separation of the vanadium from other mineral substances which are dissolved at the same time, such as oxides of uranium, aluminium and iron, and silica.

The extraction processes may be roughly classified into (1) those involving the use of acids as solvents, (2) those employing alkaline solvents. In the opinion of many authorities, it is preferable to use the latter, where possible, as the alkaline vanadates, thus obtained, are less erratic in their behaviour than are the vanadyl compounds, which result from treatment with acid. The relative merits of the two types of process are discussed by S. Fischer, *Met. and Chem. Eng.*, 1912, 10, 469. In the following notes the description of the extraction processes has been divided into sections—(1) acid extraction processes, (2) alkaline extraction processes, (3) methods of recovering the vanadium from the extraction solution. These are followed by an account of the manufacture of ferro-vanadium from the compounds isolated.

**Acid Extraction Processes.**—The Koenig method, as described in United States Patent, No. 986,180, is stated to be suitable for roscoelite, vanadiferous sandstone, and similar minerals. The crushed ore is treated with a 20 per cent. solution of sulphuric, hydrochloric, or other acid, in a rotating drum; the temperature being kept at about 200° C., and the pressure at 225 lb. per square inch. After undergoing this treatment for several hours, the solution is filtered and evaporated to a semi-solid condition. The salts are then heated to bright redness in order to expel the remaining acid. The solid residue of oxides and sulphates (if sulphuric acid were used in the first stage) is mixed with sodium carbonate, and roasted at a red heat in an oxidising atmosphere, with or without the addition of oxidising agents. The roasted mass is next treated with boiling water and then with carbon dioxide in order to precipitate any aluminium compounds present.

In the Fleck method (United States Patent, 880,645 of 1908), as used by the American Rare Metals Co. of Denver, Colorado, for the treatment of carnotite and

other vanadiferous ores, the finely-crushed ore is treated with dilute sulphuric acid, which dissolves the uranium, vanadium, copper, and iron present. The clear solution is decanted and treated with sulphur dioxide gas in order to reduce the iron and vanadium compounds to the ferrous and vanadous states. A calculated quantity of ground limestone is then added until the metals begin to separate. The solution is filtered from the precipitated calcium sulphate, and the precipitation of the metals completed by boiling the solution with more limestone. The precipitate, thus obtained, which contains about 20 per cent. of uranium and vanadium oxides, is dried and shipped for further treatment.

The process described by P. Auchinachie in English Patent, 12,726 of 1904, consists in treating the ore, for about two hours, with hot concentrated sulphuric acid to which a small quantity of sodium nitrate has been added. The acid solution, after cooling, is electrolysed, using iron electrodes, vanadic oxide being deposited. In English Patent, 22,422 of 1904, the same inventor obtains the suboxide by nearly neutralising the above acid solution with sodium carbonate and boiling for some time. The pentoxide ( $V_2O_5$ ) is obtained from this lower oxide by boiling it with sulphuric acid and sodium nitrate.

Another acid treatment process has been described by J. Ohly (*Osterr. Zeit. für Berg und Hüttenwesen*, 1906, 54, 232). It is intended for the preparation of ammonium vanadate from carnotite-bearing sandstone. The finely ground ore is treated for some time with cold hydrochloric, sulphuric, or nitric acid and then heated until all the vanadium compounds are dissolved. A predetermined quantity of ammonium chloride is added to the solution, which is next evaporated to about one-third of its bulk and left to stand over-night. The separated ammonium metavanadate is recrystallised from a concentrated solution of ammonium chloride. A further crop of ammonium metavanadate is obtained from the mother liquor by further evaporation. The final liquid is treated with excess of sodium carbonate, boiled for half an hour, the precipitate filtered off, and the uranium in the filtrate then precipitated by the addition of caustic soda.

In the Saklatwalla process (United States Patents, Nos. 1,020,224 and 1,020,312 of 1912; English Patent, No. 6,119 of 1912) the ore is extracted with dilute sulphuric acid and, after nearly neutralising the solution, the vanadium is precipitated by adding an oxidising agent, such as ammonium persulphate, chlorine, or an oxy-acid of chlorine.

According to U.S. Patent, 890,584 of 1908, ore containing uranium and vanadium is treated with sulphur dioxide under pressure and the clear solution then boiled to remove the excess of the gas. This latter treatment causes the precipitation of the uranium as basic sulphite and the vanadium is precipitated from the residual solution as calcium vanadate, by adding excess of caustic lime.

**Alkaline Extraction Processes.**—In the majority of these methods the object is to produce soluble sodium vanadate, either by treating the ore with solutions of sodium carbonate or hydroxide, or by roasting it with sodium chloride. Almost without exception, the extraction of the vanadium is not complete, but in some cases it reaches 90 per cent. of the quantity present in the ore. Roasting the ore with sufficient sodium chloride to form sodium pyrovanadate is covered by United States Patent, 831,280 of 1906.

The Primos Chemical Co., of Newmire, Colorado, employ the following process for recovering vanadium from roscoelite. The ore is mixed with common salt, the mixture coarsely ground and dried until its moisture content is about 1 per cent. The caked material is ground to pass a 20-mesh sieve and then roasted for three hours. The roasted mass is next lixiviated with water and the vanadium precipitated, as ferrous vanadate, by the addition of excess of ferrous sulphate. No attempt is made to recover the small quantity of uranium present.

In the Herreschmidt process (French Patent, 328,421 of 1903) vanadinite is fused with an alkali carbonate, sulphate, or sulphide and carbon. In a later communication (*Comptes rend.*, 1904, 139, 635) the author describes the process more fully. The vanadinite is smelted with sodium carbonate in a reverberatory furnace, and thus are produced argentiferous lead and a slag carrying vanadate, aluminate, and silicate of sodium, and ferric oxide. Air is blown through the slag in order to fully oxidise the sodium vanadate, and the mass is then granulated by pouring it into boiling water. The solution obtained by agitating the fused mass with two further quantities of water contains all the sodium vanadate, some sodium silicate, but no aluminate. To remove the silicate, one portion of the liquid is evaporated to a syrup, sulphuric acid, 66° Bé., added to precipitate a portion of the vanadic acid, and then the whole added to the unevaporated portion of the liquid. The solution is next passed through a filter press in order to remove the precipitated silica (see French Patent, No. 334,333 of 1903, and United States Patent, No. 787,758 of 1905). The solution which contains fairly pure sodium vanadate is evaporated to expel excess of sulphuric acid, and the residue, after washing with water, consists of fairly pure vanadic acid. The yield is stated to be from 92 to 95 per cent.

The above process has been employed on a large scale for treating the ore from the Santa Marta mines of Spain.



In the Haynes and Engle process, as described in United States Patents, Nos. 808,839 and 828,850 of 1906, the ore crushed to 12 mesh is boiled with a solution of sodium or potassium carbonate until the uranium and vanadium are dissolved. The length of time of boiling and the concentration of the alkaline carbonate solution are, to some extent, determined by the quantity of vanadium and uranium in the ore, and it is stated that for each 1 per cent. of these metals in the ore, about 100 lb. of sodium carbonate is required per ton of ore. The clear solution is treated with sodium hydroxide to precipitate the uranium as sodium uranate, which is then removed by filtration. The vanadium is next precipitated from the filtrate by the addition of slaked lime. When used on carnotite ore, this process gave an extraction of about 80 per cent. of the uranium and 60 to 65 per cent. of the vanadium present in the ores.

According to the process described by A. H. Perret (French Patent, No. 412,641 of 1901, and English Patents, 26,777 of 1910, and 15,181 of 1911) the ore is roasted with an alkaline carbonate and oxidising conditions maintained after the addition of sodium nitrate. The fused mass is granulated by being run into cold water and thoroughly lixiviated. The solution, which contains all the vanadium, may be treated with ammonium chloride so as to give ammonium metavanadate or the vanadic acid may be precipitated by the addition of an acid.

It was stated recently that a large works in France had been acquired by the Santa Marta Co. of Spain in order to treat their ore by this process.

In addition to the processes already described for the separation of uranium and vanadium on a technical scale, that of W. F. Bleecker must be mentioned. As described in United States Patent, 1,050,796, the process consists in treating the alkaline carbonate solution with sufficient sodium hydroxide to precipitate the uranium as a mixture of uranyl hydrate and sodium uranate. This precipitate, which contains some vanadium, is filtered, washed, dissolved in acid, and the solution treated with excess of sodium carbonate. The solution is then electrolysed, using anodes of any active metal, such as iron, nickel, or copper, the vanadium being precipitated on the anode as vanadate of the anode metal. When all the vanadium has been deposited the uranium in the filtrate may be recovered by one of the known methods.

A method for extracting vanadium from copper vanadate is described by W. F. Bleecker in United States Patent, 1,049,330.

**Methods of Recovering the Vanadium from Mill Solution.**—A number of the processes already described have included details of the method of recovering the uranium and vanadium from the extraction or "mill" solutions. These may be briefly summarised as consisting in precipitation (1) as ferrous vanadate by nearly neutralising the solution, and adding ferrous sulphate; (2) as calcium vanadate by the addition of slaked lime; (3) by electro-deposition.

In the first-mentioned process several difficulties may be encountered, thus, according to W. F. Bleecker (*Met. and Chem. Eng.*, 1911, 11, 501), sodium sulphate, formed by the interaction of the sodium carbonate and ferrous sulphate, is a powerful solvent for ferrous vanadate unless the ferrous sulphate is present in considerable excess. A small amount of a colloidal compound is formed, which causes difficulty in washing the precipitate, and loss of vanadium. Calcium vanadate would seem to suffer from few of the above objections.

**Electrolytic precipitation** appears to possess several advantages over the foregoing methods. In all hydro-electrolytic processes vanadium is always an anode product, and so, if ferrous vanadate is required, the nearly neutral solution containing the vanadium is electrolysed, using iron anodes and cathodes of almost any metallic substance. A potential difference of about 4 volts is maintained between the electrodes. As a rule, any impurity present in the solution is found, in part at least, in the final product. For a discussion of the process, see W. F. Bleecker, *loc. cit.*

**Vanadic Acid** may be prepared from the solution of sodium vanadate, by treatment with acid as already described, but this process does not precipitate all the vanadium; some 10 per cent. remaining in solution. An electrolytic process, described by W. F. Bleecker, takes advantage of the difference in solubility of sodium vanadate and vanadic acid.

The solution of sodium vanadate, which must not contain chlorides, is heated to 90° C., and then made slightly alkaline with sodium carbonate. The clear liquor is decanted, evaporated to 30° Bé., when it will contain about 200 gm. of vanadic acid per litre. This solution is transferred to a porous pot, and electrolysed in a compartment cell, the liquid in the outer jar being water containing a little lye. A platinum anode is used, whilst the cathode may consist of iron or copper. A potential difference of 6 to 8 volts is maintained together with a current density of 30 amperes per square foot of anode surface. The effect of the current is to cause the sodium ions to travel to the outer vessel, leaving vanadic acid in the inner porous pot. As this salt is less soluble in water than is sodium vanadate, a portion of it is precipitated. The product obtained, in this way, is easily filtered and washed, and contains about 98 per cent. of vanadic oxide ( $V_2O_5$ ). Mineral acids seriously interfere with the efficiency of the reaction.

The oldest process for obtaining vanadic acid is that of preparing ammonium metavanadate, and then driving off the ammonia by heating.

When dry calcium vanadate is treated with hot hydrochloric acid, red vanadic acid separates out, which can be washed with dilute acid and water.

The product always contains some lime salts, and a considerable quantity of hydrochloric acid is present as vanadyl dichloride. If the material be dried and fused a practically pure sample of vanadic oxide ( $V_2O_5$ ) will be obtained.

**Metallic Vanadium** may be produced according to G. Gin (*Elektrochem. and Met. Ind.*, 1909, 7, 264) by the electrolysis of a solution of vanadium trioxide ( $V_2O_3$ ) in fused calcium vanadate.

The lining of the bath in which the electrolysis is performed is pure electrolytically fused alumina. The anodes are composed of carbon, whilst the cathodes are conical in form, and consist of pulverised and agglomerated ferro-vanadium. A current density of about 4.5 amperes per square inch of anode is recommended.

The metal may also be prepared by the aluminothermic method (see W. Prandtl and B. Bleyer, *Zeits. anorg. Chem.*, 1909, 64, 217, and *Ber.*, 1910, 43, 2602, and R. Vogel and G. Tammann, *Zeits. anorg. Chem.*, 1909, 64, 225).

**Ferro-Vanadium.**—The processes available for the production of this substance are the reduction of ferrous vanadate, calcium vanadate, or the oxides by means of (1) carbon in the electric furnace; (2) the aluminothermic process.

Alloys produced by the first method usually contain somewhat large amounts of carbon (1.5 to 6 per cent.), which renders the alloy objectionable for certain uses in the steel industry.

For the aluminothermic process, it has been stated that the lower oxide ( $V_2O_3$ ) is more suitable. The majority of the ferro-vanadium now on the market contains from 25 to 50 per cent. of vanadium.

In the Gin electrolytic process for the production of ferro-vanadium from vanadic acid, as described in *Zeits. Elektrochem.*, 1903, 9, 831, electrodes prepared from a mixture of vanadic acid and retort carbon are used as the anode in a bath of fused iron fluoride dissolved in fused calcium carbide, whilst fused steel constitutes the cathode.

In French Patent, 340,413 of 1904, the electrolyte is composed of fused calcium fluoride, but iron fluoride is also added, as the decomposition of this latter substance assists the process by regenerating the electrolyte at the expense of the anode.

In a later communication (*Proc. 7th Inter. Cong. Appl. Chem.*, 1909, Sect. 10, p. 10) the same inventor suggests the use of vanadic acid dissolved in fused calcium fluovanadate. A carbon anode is used, whilst the cathodes consist of agglomerated carbon and vanadic acid as before. A current density of 0.7 ampere per square centimetre of anode surface is stated to be the most suitable.

Ferro-vanadium may be prepared, according to United States Patent, 866,561 of 1907, by passing an electric current through a bath of molten ferro-silicon and vanadic oxide in calculated amounts.

According to United States Patent, 875,208 of 1907, ferro-vanadium is prepared by mixing the oxide with the calculated amounts of iron and carbon and passing a current through the charge.

**Composition of Vanadium Alloys.**—As already stated, ferro-vanadium made by the reduction of vanadium compounds by means of carbon contains from 2 to 6 per cent. of the latter element, and has not the same utility, in the steel industry, as those alloys with under 1 per cent. of carbon.

The reason for this is stated to be that vanadium readily combines with carbon, to form a carbide which is a stable product and passes into solution in the steel without decomposition, and is stated, therefore, to be of much less value for use in the steel industry.

The melting point of a ferro-vanadium, practically free from other elements, and containing 40 per cent. of vanadium, is about 1480° C. The melting point becomes gradually lower as the amount of vanadium is decreased until 35 per cent. is reached, when it remains stationary at 1425° C. until 30 per cent. is attained. From this point, as the vanadium is decreased to 25 per cent., the melting point gradually rises to about 1450° C.

Most firms supply several grades of ferro-vanadium, of different vanadium content.

The amounts of certain elements in commercial ferro-vanadium are shown in the following table :—

TABLE XXVII

	Per Cent.	Per Cent.	Per Cent.	Per Cent.	Per Cent.
Vanadium	20 to 25	25 to 30	30 to 40	35 to 42	30 to 40
Silicon	1.5 to 3.0	Below 2.0	Below 2.0	Below 2.0	1 to 3
Carbon	4 to 6	0.25	0.25	0.25	...
Aluminium	Below 0.05	Below 2.0	Below 2.0	Below 1.0	...
Manganese	6 to 8	...	...	...	...

Cupro-vanadium may have the following percentage composition—vanadium, 10 to 15 ; copper, 60 to 70 ; aluminium, 10 to 15 ; nickel, 2 to 3.

### Utilisation of Vanadium and its Salts

At least 90 per cent. of the vanadium extracted is utilised in the form of its ferro alloy, in the steel industry ; a use which has gradually increased during the past ten years. A very complete account of the use of vanadium and its alloys in steel-making has been given by J. Kent-Smith (*Journ. Soc. Chem. Ind.*, 1906, 25, 291). Briefly summarised, the effect of vanadium on steel may be stated as being to increase the elastic limit and ultimate tensile stress without reducing the ductility.

It is chiefly employed in connection with the manufacture of chrome, manganese, open hearth and high speed tool steels, being especially useful in the production of steel required for use in the construction of motor cars, steel shafts, locomotive axles, rock drills, and similar work subject to shock. Vanadium is stated to toughen steel in several ways, such as (1) by causing any oxides and nitrides present in the steel to pass into the slag ; (2) the metal passes into solid solution in the ferrite or carbonless portion of the steel rendering the metal more coherent and less liable to disintegration. The quantity of vanadium required for the first-mentioned effect rarely exceeds 0.1 per cent. of the weight of steel treated.

The total quantity of vanadium added to ordinary engineering structural steels usually amounts to about 0.25 per cent., whilst as much as 2.0 per cent. may be added to high quality tool steels.

For further details see J. O. Arnold and A. A. Read, *Trans. Iron and Steel Inst.*, 1912, 85, 215 ; P. W. Shimer, *Trans. Amer. Inst. Min. Eng.*, 1912, 883.

Copper-vanadium alloys are much used in the production of solid copper castings and bronzes, as well as in the manufacture of certain aluminium alloys.

A number of uses have been suggested for vanadium compounds, but it would appear that few of these demand any large quantity of material.

In **Photography**, vanadium salts have been used for toning silver-bromide prints to a green colour. According to German Patent, 215,071 of 1909, and U.S. Patent, 979,887 of 1910, when 500 gm. of liquid vanadium chloride is mixed with 1,310 gm. of anhydrous oxalic acid, a solid product is obtained which may be compressed into tablets and is readily soluble in water. The toning bath is prepared by dissolving 3.8 gm. of this product together with 1.5 gm. of anhydrous oxalic acid, 1 gm. of ferric oxalate, and 1 gm. of potassium ferri-cyanide in one litre of water. The photographic properties of vanadium salts are discussed by L. Lumière in *Moniteur Scientifique*, 1894, 42, 437.

The use of vanadium or its alloys in place of lead in **accumulators** has been patented (French Patent, 357,601 of 1905), and in the same specification it is mentioned that solutions of vanadium salts may replace sulphuric acid in accumulators.

Vanadium salts have been used for colouring **pottery** and **glass**, and the pentoxide ( $V_2O_5$ ) has been suggested for use as a "gold bronze."

Vanadium salts are employed as **mordants**, for fixing aniline black on silk, and in calico printing. The use of ammonium vanadate in dyeing leather is described in *Journ. Soc. Chem. Ind.*, 1882, 1, 185.

When solutions of vanadium salts are mixed with tincture of galls, a deep black colour is produced, and it has been suggested that the solution might be employed as a **writing ink**. It has been shown, however, that although the colour is unaffected by acids, alkalies, or chlorine, it is not permanent.

**As Catalysts**, oxides of vanadium may be employed in the electrolytic oxidation and reduction of certain organic compounds (see French Patent, 345,701 of 1904). It is also stated to accelerate ordinary oxidation (see A. Naumann, L. Moeser, and E. Lindenbaum, *Journ. prakt. Chem.*, 1907,

75, 146). Vanadium carbide has been suggested as a filament for incandescent electric lamps (English Patent, 19,264 of 1905). In medicine, certain vanadium salts find a limited use.

### Chemical Analysis of Vanadium Ores and Alloys

Space does not permit of an account being given of a method for the analysis of complex vanadium ores, but the following "Rapid Method for the Determination of Vanadium in Ores," as given in *United States Geol. Survey, Bull.* 70, p. 90, may be of service. It is suitable for ores which are readily attacked by acid.

Treat 2 to 5 gm. of the ore in a 16-oz. Erlenmeyer flask with 20 c.c. of hydrochloric acid (sp. gr. 1.20), and warm for half an hour. Add 20 c.c. of water and 20 c.c. of sulphuric acid, and evaporate till fumes of sulphuric acid are liberated. While the mixture is hot, add powdered potassium permanganate, a little at a time, until all organic matter is oxidised and an excess of permanganate is present. Heat for a few minutes, cool, and add 25 c.c. of water and a few drops of a strong solution of potassium permanganate to ensure complete oxidation. Add 50 c.c. of hydrochloric acid (sp. gr. 1.20), and evaporate as rapidly as possible, without causing "bumping," until the hydrochloric acid is expelled and sulphuric acid fumes are evolved. Continue the fuming for ten minutes. Cool, add a little cold water, dilute to 250 c.c. with boiling water, and determine the vanadium by titrating the hot solution with a standard solution of potassium permanganate.

In most cases it is unnecessary to remove the insoluble matter; sometimes, however, it is advisable to do so. Place the ore in a beaker, add 10 c.c. of hydrochloric acid and 5 c.c. of sulphuric acid, evaporate till fumes of the latter are liberated, take up with water, and filter into the flask. Then add 15 c.c. more sulphuric acid, and proceed as above.

If arsenic and molybdenum are present, they may be removed from the dilute sulphuric acid solution before filtration by precipitation with sulphuretted hydrogen.

Success with this method depends upon complete destruction of the organic matter and complete oxidation of the iron, etc., by potassium permanganate. Some vanadium ores contain much organic matter. In treating these the sulphuric acid solution should be heated longer, and several cautious additions of powdered potassium permanganate should be made. In some cases preliminary calcination at a low temperature will save time. Several other methods are also given in the above-mentioned bulletin.

A comprehensive account of the analysis of vanadium ores of all types is given by W. F. Bleecker in *Met. and Chem. Eng.*, 1911, 9, 209, whilst the methods suitable for ferro-vanadium are discussed by W. W. Clarke, *Met. and Chem. Eng.*, 1913, 11, 91.

Thanks are due to the **International Vanadium Co.**, of Liverpool; **The American Vanadium Co.**, of Pittsburgh, U.S.A.; and **The Primos Chemical Co.**, of Primos, Delaware Co., U.S.A., for supplying certain information concerning the uses of vanadium salts and alloys.

## CHAPTER IX

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### The Industry of Radioactive Substances



# CHAPTER IX

## THE INDUSTRY OF RADIO-ACTIVE SUBSTANCES

By ALEXANDER S. RUSSELL, M.A., D.Sc.,  
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### LITERATURE

- E. RUTHERFORD.—“Radioactive Substances and their Radiations,” Cambridge University Press, 1913. This is the best book on Radioactivity.
- F. SODDY.—“The Chemistry of the Radio-elements,” Longmans, Green, & Co. Part I. (new edition), 1915. Part II., 1914. These books deal thoroughly with the chemical aspect of Radioactivity.
- J. JOLY.—“Radioactivity and Geology,” Archibald Constable & Co., 1909. This work deals with the distribution of radium, etc., in the earth’s crust, and gives in detail methods for detecting radium in minerals, waters, muds, etc.
- C. A. PARSONS, in an article in *Science* (31st October 1913), gives a valuable account of the radium resources of the world.
- E. T. WHERRY.—“Carnotite near Mauch Chunk.” *Bull.* 580-H., *U.S. Geol. Sur.*, Washington, 1914.
- E. EBLER and W. BENDER.—“Preparation of Radium.” *Zeits. anorg. Chem.*, 1914, 88, 255-264.
- BULLETIN 70, issued by the Bureau of Mines, Department of the Interior, Washington, U.S.A., 1913. This bulletin deals with the uranium, radium, and vanadium resources in the Western States.
- RADIUM.—Report presented to the House of Representatives, U.S.A., see *Chem. News*, 1914, 110, 264-266, 276-278, 284-286, 301-302, 310-312; see also *Journ. Soc. Chem. Ind.*, 1913, 616, 1066, 1107.

THE following are the chief recent patents relating to the extraction, preparation, and use of radioactive materials:—

- British*.—20,922, 1902; 11,926, 1905; 24,222, 1906; 14,760, 1909; 19,820, 1909; 25,504, 1910; 778, 1911; 14,471, 1911; 21,462, 1911; 8,908, 1912; 20,081, 1912; 24,887, 1912.
- United States*.—787,928, 1905; 788,480, 1905; 895,478, 1908; 907,066, 1908; 917,191, 1909; 1,076,141, 1913; 1,065,581, 1913; 1,065,582, 1913; 1,084,734, 1914; 1,100,743, 1914; 1,103,600, 1914.
- French*.—370,749, 1906; 386,751, 1908; 406,299, 1908; 411,099, 1909; 411,629, 1909; 416,588, 1910; 418,455, 1909; 429,368, 1911; 440,236, 1912; 440,127, 1912; 440,236, 1912; 455,189, 1913; 459,081, 1913; 456,990, 1912; 466,015, 1913; 466,850, 1913; 467,330, 1914.
- German*.—226,804, 1909; 264,901, 1912; 256,666, 1912; 269,541, 1911; 269,692, 1912; 274,874, 1913.

## INTRODUCTION

**History.**—The discovery of X-rays by Röntgen in 1895 called attention to the study of other obscure radiations. Becquerel, between 1895-1903, discovered the fact that uranium salts gave invisible rays which affected a photographic plate in the dark. In 1898 G. C. Schmidt and Madame S. Curie discovered that thorium salts acted in a similar way, and this led to the discovery of the radioactive elements, polonium and radium.

In 1902 Geoffrey Martin (*Chem. News*, 1902, 85, 205) put forward the theory that the radioactive elements are elements undergoing decomposition—the theory now universally accepted but received at the time of its publication with open ridicule. Rutherford and Soddy, later in the same year, adopted the same view, which was put on a firm experimental basis by their classical researches. The evolution of helium from radium was first proved by Ramsay and Soddy in 1903. Radium emanation was first recognised as a gas by Rutherford and Soddy in 1902. Fajans, Russell, Fleck and Soddy in 1913-1915 established the position of the radioactive elements in the periodic system.

There are few departments of technical chemistry that have been more neglected in Great Britain than technical work in connection with the radium industry. Part of this neglect has its origin in the reception given by some prominent chemists in England to the chemical aspect of the pioneer work on radioactivity carried out by Rutherford and his colleagues in 1902 and the years that followed. The subject was regarded in many quarters as fantastic, speculative, unsafe, and of no importance, and it was generally taken for granted that any work that might be done in it could be conveniently left to physicists who possessed a knowledge of inorganic chemistry. The second and more important reason has been the great difficulty of obtaining in this country, either cheaply or in any quantity, the raw material from which the more important radioactive constituents could be worked up. The uranium ores are by no means plentiful in amount, and are only found in certain parts of the world. Again, immediately after its discovery radium was surrounded by a halo of romance by the press of England and the Continent. A substance which had hitherto been of theoretic interest only, and of little use practically, was then declared to be a body likely to be of the highest practical value in the future. This speculative pronouncement had the effect of preventing workers from putting it to any practical use. The fortunate possessors of the raw material from which this substance could be extracted did what most people do with a thing that attracts general attention, they proceeded to make as much money out of the material as they could so long as it held the public mind. The result has been that the prices of raw material and of purified material alike have risen continuously, until at the present time only those who have large sums of money at their back are able to obtain possession of it.

Radium, mesothorium, or any other radioactive substance should never be bought without a guarantee as to its genuineness, its purity, and its amount. This can now be easily obtained at the National Physical Laboratory at Teddington, in England.

## RADIOACTIVE ELEMENTS

It is necessary, for the better understanding of what follows, that a short account be given here of the theoretical work on radioactivity, in so far as it is necessary to explain things of a technical nature. The reader is referred to Rutherford's book for a full account.

Radioactivity is an atomic phenomenon. The radioactivity of a radium atom, for instance, is due to the element, radium, itself, and to that alone. It is in no



way increased or decreased when that element is chemically combined with other atoms. It is neither diminished nor increased in the least degree by subjecting the body to any change of pressure or of temperature. Radioactivity is due to the expulsion of certain **radiations**, which are conveniently grouped under three heads according to their penetrating power. The least penetrating of the three is the  **$\alpha$ -particle**, or, as it was formerly called, the  **$\alpha$ -ray**.

This radiation or particle possesses two positive charges of electricity, and is expelled by different radioactive atoms with different velocities, all of which, however, are of the order of one-tenth of the velocity of light. This particle has been definitely proved to have an atomic weight of about four, and is indeed a charged atom of helium.

The most penetrating radiation is called the  **$\gamma$ -ray**.  $\gamma$ -rays are of the same nature as X-rays, but many of the  $\gamma$ -rays, though not all, expelled by radioactive bodies, are much more penetrating than any known X-ray.

The most penetrating  $\gamma$ -rays, namely, those from mesothorium, thorium D, and from radium C, are so penetrating that more than a centimetre of lead is required to reduce the radiation to half its value. The intensity of the radiation is reduced in geometrical progression, as the thickness through which it has to pass is increased in arithmetical progression. Thus, if a centimetre and a half of lead reduce a radiation to 50 per cent. of its former intensity, three centimetres will reduce it to 25 per cent., four and a half centimetres will reduce it to  $12\frac{1}{2}$  per cent., and so on. It is thus possible to detect the  $\gamma$ -rays from radium after they have passed through twenty centimetres of lead. Other bodies absorb these penetrating rays directly in proportion to their density. Thus, aluminium has roughly one-fifth the density of lead. Therefore a sheet of the latter metal must be five times the thickness of one of the former in order to produce an equivalent reduction in the strength of a given radiation.

The rays of intermediate penetrating power are called  **$\beta$ -rays**. They are of the same nature as the electrons or cathode rays which are produced in a vacuum tube by a discharge.

They possess one negative charge of electricity, and are expelled with a velocity varying in magnitude from about 20 to 99 per cent. of the velocity of light. They are able to penetrate up to about three millimetres of aluminium, and proportionate thicknesses of other metals and bodies.

There are at present considerably over thirty bodies which expel one or more of these three types of radiations. Each of these bodies is an element with definite chemical properties, and with an absolutely definite existence.

A radioactive element differs in no way either in its chemical or physical properties from those of any common element. It possesses, however, in addition, one property which common elements do not possess, namely, that in a given interval of time a certain definite proportion of the total number of atoms of the radioactive element break up or disintegrate with the expulsion of  $\alpha$ ,  $\beta$ , or  $\gamma$  rays. It is **the atom** which disintegrates. The atom, after the expulsion of the radiation, is obviously different in nature to what it was before. It is a new atom, and the whole of the atoms, which are the resultant of this expulsion, form a new element. This may be made plainer by taking an actual case. The atomic weight of the element, uranium, is 238.5. In any given interval of time a definite percentage of the total number of atoms of uranium present disintegrate. The radiation expelled in this case is an  $\alpha$ -particle, which has an atomic weight of 4. The resultant atom is entirely different in nature from the uranium atom. It is to be expected that a disturbance inside the atom itself, which has resulted in the expulsion from it of a particle of this magnitude, has disarranged the structure of the atom sufficiently to give it different chemical and physical properties. The atomic weight of the new atom is also four units less than the parent atom. In this particular case the resultant atom is called uranium X. Its atomic weight is 234.5, and its chemical properties resemble very closely those of thorium. It is therefore easily separated from uranium.

Every radioactive element except uranium, thorium, and actinium is the resultant or product of some one radioactive element, and every radioactive element is the parent of some one other element.

Uranium, thorium, and actinium are called **primary radioactive bodies**. They are not the products of any element known. They form the heads of the three **disintegration series** of radioactive bodies.

A **disintegration series** is simply an arrangement of elements in which every body is the product of the one coming before it, and the parent of the one following it.

The four things which are of interest in any radioactive body are—

- (1) *What is its period of average life?*
- (2) *What type of radiation does it emit?*
- (3) *Into what body does it disintegrate?*
- (4) *What are its chemical properties?*

The first of these requires some explanation. It has been stated above that in any interval of time a definite fraction of every radioactive body disintegrates forming a new body. This fraction is different for each body.

If  $I_0$  be the number of atoms of any disintegrating body originally present,  $I_t$  the number after a time  $t$  has elapsed,  $I_0$  and  $I_t$  are connected by the equation—

$$I_t = I_0 e^{-\lambda t},$$

$$i.e., \quad \frac{\log I_0 - \log I_t}{.434t} = \lambda.$$

$\lambda$  is the **disintegration constant**. It is always determined experimentally.  $\frac{1}{\lambda}$  is called the **period of average life** of the atoms of the body.

Any body which disintegrates or decays according to the equation above does so at such a rate that at the end of a certain interval of time there is one-half of the number of atoms present which there were at the commencement of the interval. This interval is called the **half-value period**. The **period of average life** of any body is 1.443 times the half-value period.

In the following tables are tabulated the members of the three disintegration series, the radiations emitted by them, their periods of half-value, and their chemical properties. The chemical properties are for shortness expressed in terms of those of common elements.

#### A. THE URANIUM SERIES

Name of Element.	Symbol.	Radiation Emitted.	Half-Value Period.	Common Body Possessing Chemical Properties Most Similar.
Uranium 1	Ur1	$\alpha$	$5 \times 10^8$ years	Uranium
Uranium X <sub>1</sub>	UrX <sub>1</sub>	$\beta, \gamma$	24.6 days	Thorium
Uranium X <sub>2</sub>	UrX <sub>2</sub>	$\beta, \gamma$	1.15 mins.	Tantalum
Uranium 2	Ur2	$\alpha$	About $10^8$ years	Uranium
Ionium	Io	$\alpha$	About $2 \times 10^5$ years	Thorium
Radium	Ra	$\alpha, \beta$	2,000 years	Radium
Radium emanation	RaEm	$\alpha$	3.85 days	(Inert gas)
Radium A	RaA	$\alpha$	3.0 mins.	Tellurium
Radium B	RaB	$\beta, \gamma$	26.8 mins.	Lead
Radium C	RaC	$\alpha, \beta, \gamma$	19.5 mins.	Bismuth
Radium D	RaD	$\beta, \gamma$	16.5 years	Lead
Radium E	RaE	$\beta$	5.0 days	Bismuth
Polonium	Po	$\alpha$	136 days	Tellurium

## B. THE ACTINIUM SERIES

Name of Element.	Symbol.	Radiation Emitted.	Half-Value Period.	Common Body Possessing Chemical Properties Most Similar.
Actinium	Act	None	Unknown	Lanthanum
Radio actinium	RaAct	$\alpha, \beta, \gamma$	19.5 days	Thorium
Actinium X	ActX	$\alpha$	10.2 days	Radium
Actinium emanation	ActEm	$\alpha$	3.9 secs.	Radium emanation
Actinium A	ActA	$\alpha$	0.002 sec.	Tellurium
Actinium B	ActB	$\beta$	36 mins.	Lead
Actinium C	ActC	$\alpha$	2.1 mins.	Bismuth
Actinium D	ActD	$\beta, \gamma$	4.71 mins.	Thallium

## C. THE THORIUM SERIES

Name of Element.	Symbol.	Radiation Emitted.	Half-Value Period.	Common Body Possessing Chemical Properties Most Similar.
Thorium -	Th	$\alpha$	About $1.3 \times 10^{10}$ years	Thorium
Mesothorium 1	MsTh1	None.	5.5 years	Radium
Mesothorium 2	MsTh2	$\beta, \gamma$	6.2 hrs.	{ Actinium and Lanthanum
Radiothorium	RaTh	$\alpha$	2 years	Thorium
Thorium X	ThX	$\alpha, \beta$	3.65 days	Radium
Thorium emanation -	ThEm	$\alpha$	54 secs.	Radium emanation
Thorium A	ThA	$\alpha$	.14 sec.	Tellurium
Thorium B	ThB	$\beta, \gamma$	10.6 hrs.	Lead
Thorium C	ThC	$\alpha, \beta, \gamma$	60 mins.	Bismuth
Thorium D	ThD	$\beta, \gamma$	3.1 mins.	Thallium

One or two alterations of a minor character would require to be made in the above tables to represent the present state of knowledge. The omissions relate to branch products. These products, however, are of no practical interest. Each body described above is the parent of the body following it in the table.

Except in the case of thorium A and actinium A, the chemical properties of all the radio-elements have been determined experimentally. A rule has also been found (Soddy, *Chem. News*, 1913, vol. 107, p. 97) by means of which, from a knowledge of the chemical properties of an element, and the radiations expelled by it and by all its products, the chemical properties of any subsequent member of its disintegration series can be predicted. These predictions in every case agree with the experimental results. It will be seen from the tables that radium B, thorium B, and actinium B are all described as being similar in chemical properties to lead.

The property of radio-elements, being very similar in chemical properties to common elements, is one of the most extraordinary phenomena in the subject, but it is a thing that greatly simplifies chemical work. Thorium B, for instance, is so similar to lead that there is no known method of separating one from the other, or of even concentrating one in a mixture of both in the least degree. To separate thorium B from other radioactive bodies, therefore, one requires only to add a trace of lead to the active solution, and separate the lead by ordinary methods. It will be found that thorium B is separated quantitatively with it, and is free from all other radioactive bodies except those which have the same chemical properties as lead, or which have grown from the thorium B between the time of separation and the time of examination. The same principle can be applied to separate other radioactive elements.

A body is said to be *in equilibrium* with its product when the ratio of the amount of the product to that of the parent body remains constant with time. In

such a case the amount of the product produced by the transformation of the parent substance in any time must equal that transformed into a third body. If a product be wholly removed from its parent substance, it grows again in the parent body according to an exponential law with the time which is independent of the period of the parent substance (unless the period be very short), and depends on the half-value period of the product grown.

Thus if radium emanation be removed from a solution of radium it decays to half-value every 3.85 days, that is to say in 7.70 days there is only 25 per cent. of the original quantity of emanation left, after 11.55 days only 12½ per cent., and so on. But in 3.85 days 50 per cent. of the equilibrium quantity of radium emanation has formed again in the radium solution, 75 per cent. in 7.70 days, 87½ per cent. in 11.55 days, and so on, the rate at which the emanation forms in the solution depending only on the half-value period of radium emanation and not on that of radium itself.

### Radioactive Bodies of Technical Importance

It is clear that only bodies of reasonably long periods can be of technical importance. These are **radium**, **mesothorium 1**, **radiothorium**, **radium D**, **polonium**, and **ionium**.

It will be noticed that four bodies of long period have been omitted, viz., **uranium 1** and **uranium 2**, **thorium** and **actinium**. The reason for the omission of the first three is that they are too inactive to be of importance, that is to say, the proportion of the number of atoms of any of these bodies breaking up per hour to the total number is so small that they are of no practical use. The reason for the omission of actinium is due to the fact that no one has yet succeeded in concentrating it from the large mass of lanthanum which associates with it in the process of separating actinium from a mineral. Were this possible, actinium would be a body of some technical importance.

The second and third of the six bodies named above belong to the thorium series, the other four to the uranium series. The sources of these six bodies are therefore the sources of the two elements, thorium and uranium.

### Sources of Thorium

The chief sources of the element thorium at the present time are the **monazite sand** deposits of Brazil, Travancore, and North and South Carolina (see under **Thorium**, p. 4). Practically the whole of the thorium used for making incandescent gas mantles is extracted from ore from these sources. As these are the best and cheapest sources known at present for this industry, they must also be the best and cheapest sources for **mesothorium** and for **radiothorium**.

The preparation of these bodies is, therefore, a by-product in the thorium industry, and any body engaged in separating thorium on a large scale can, by performing a few more chemical operations, prepare at the same time preparations of these radioactive bodies.

There is another source of **mesothorium**, but it can be used only for the production of small preparations, and that is the mineral **thorianite**.

**Thorianite** is a mineral found in Ceylon, containing about 70 per cent. of  $\text{ThO}_2$  and about 10 to 30 per cent. of  $\text{U}_3\text{O}_8$  and oxides of other rare earths (see p. 8). Were this mineral to be sold in the market at a cheap rate it would be the best source of all these bodies, for it is much more easily worked up than monazite sand. There is, however, only a small quantity of this mineral in existence, and therefore it cannot be used to extract preparations on a commercial scale.

As the **thorium industry** has been dealt with in a separate chapter of this work (p. 3), it is not proposed to deal further with it here. This can be said, however, that as long as the supplies of monazite sand are available, and there is no sign at present that they are approaching exhaustion, so long will quantities of **mesothorium** and **radiothorium** be obtainable as by-products in the industry.

### Sources of Uranium

The natural occurrence of uranium ores has already been considered (see p. 93), and it will only be necessary to consider here a few details of special interest in connection with the radium industry.

The original source of uranium, and therefore of radium and the other radioactive bodies of the uranium series of technical importance, was the **pitchblende mines** of **St Joachimsthal** which are owned and worked by the Austrian Government.

Pitchblende has been the most fruitful source of radioactive materials up to the present, and most of the radium now in use has been extracted from this ore. These deposits are now alleged to be worked out.

Originally this ore was sold at such a price that after allowing for the cost of extraction of radium, the radium could be sold at less than 10s. per milligramme of radium bromide. Gradually, however, the price of the ore rose, till at the present time a milligramme of radium bromide costs about £15, though as is well known the actual cost of extracting radium on a large scale from a high-grade ore, such as that obtained from the Austrian mines, *does not exceed 5s. per milligramme.*

With the gradual exhaustion of the St Joachimsthal mines, and the difficulty people had in obtaining, for any money at all, radium from the Austrian Government, a general search was made over the world for new deposits. The most fruitful source has been located in America, and it looks at present as if there and there alone is a chance of obtaining radium and other products in sufficient quantities to meet the demands of the world.

The **Cornwall mines** of England have been described as being good sources of radium, and two companies have been formed to extract this substance from them. It must be confessed, however, that the results have been disappointing up to the present.

Quantities of a mineral called **Autunite** (p. 94) were recently discovered in Portugal. **Autunite** is a phosphate of calcium and of uranium of great purity, when freed from the gangue with which it is associated. Much of the radium in equilibrium with the uranium, however, has been washed away from it by percolating water. There is no evidence that anything more than a few hundred milligrammes of radium bromide have been extracted from this source.

The most important ore in America, and, indeed, the most important and most fruitful ore of radium known at the present time, is **Carnotite** (p. 93).

It must be understood that the extraction of uranium ores on a large scale has only just commenced in the United States. Until a year or so has elapsed, it will not be possible for anyone to say definitely what quantity of radium can be extracted from these mines. At present we are confined to estimates made by experts on the spot. Officials from the Bureau of Mines have declared that there is enough ore in Colorado to produce at least 180 g. of pure radium. This is the lowest estimate of all. Others have placed the figure as high as 900 g.

### The Manufacture of Radium

Until recently the manufacture of radium has been carried on in France, Germany, and in Austria. Even the ore obtained from the Cornwall mines was mostly shipped to France to be worked up. In America and Australia radium is now being extracted. The essential methods of treatment are of course well known, and all that is required is the adaptation of these to the mineral carnotite, a mineral which is easier to work up than pitchblende.

A National Radium Institute, having a right to work certain claims in Denver, is already (1913) at work in conjunction with the official Bureau of Mines, and already 100 tons of high grade carnotite ore have been mined. A great deal of ore, however, is still being exported to the Continent, and there is at present so great a demand for it that carnotite ores, containing as little as one per cent. uranium oxide, find a market on the Continent.

**The Curie-Debiegne Process of Radium Extraction.**—In extracting radium from any uranium ore, the most important operations are the separation of the mineral proper from the gangue and impurities which are mined with it, the solution of the mineral, the separation of the radium with the barium of the mineral as sulphate, and, lastly, the fractionation of the barium-radium product to obtain

pure radium. The first of these is effected by mechanical or other means, which need not be discussed here. The reagent for effecting solution of the mineral depends on the particular composition of the mineral. In the case of carnotite, which is now the most abundant ore, the solvent is a dilute solution of hydrochloric acid. From this solution the bodies whose sulphates are difficultly soluble are precipitated. In these insoluble sulphates, the radium of the mineral is found in almost quantitative amount, as radium sulphate is even more difficultly soluble than barium sulphate. The sulphates are then converted into carbonates by vigorous boiling with sodium carbonate solution, filtering and washing free from sulphate. The carbonates are then treated with pure hydrochloric acid, which dissolves the alkaline earths and radium. From this solution the latter may be precipitated as sulphates by sulphuric acid, converted back into carbonates, and the carbonates dissolved again in pure hydrochloric acid. In this way barium and radium are separated from the other impurities, namely, iron, lead, and calcium, which are usually associated with it.

According to R. Sternlicht (*Chem. Zeit.*, 1914, 38, 49), pitchblende (average uranium content, 45 per cent.) is worked by this process at the Austrian State radium factory as follows:—The uranium ore is roasted, the uranium removed, and the residual sulphates of Ca, Ba, Er, and Ra which remain are converted into carbonates by boiling with concentrated  $\text{Na}_2\text{CO}_3$  solution. The carbonates are then converted into chlorides, and the radium separated by fractional crystallisation of the chlorides. The process, however, is very laborious, and yields only 80 per cent. of the original radium content.

The French factory of Armet de Lisle, however, extracts the radium directly from their uranium ore by treating with HCl. They work with materials containing only a very low percentage of radium, principally "uranium mica," "uranium ochre," carnotite, and autunite. They attain a yield of 70 per cent. radium, but the process is difficult and costly.

**The Ulzer-Somner Method of Radium Extraction** (see English Patent, 19,820, 30th August 1909).—The material containing radium is first treated with concentrated  $\text{H}_2\text{SO}_4$  for some weeks at the normal temperatures, or a few hours at a boiling temperature, or it is fused with acid sulphates; and the residue remaining after repeated washing is boiled, under pressure, with concentrated solutions of caustic alkalis or alkali carbonates, or is melted therewith; the melt is treated with water, and, after further repeated washing, the residue is boiled with dilute sulphuric acid. The same effect is attainable by treating first with alkaline agents and then with acid agents. The residue which remains (about 0.5 per cent of ore) contains all the radium as  $\text{RaSO}_4$ .

The following example is quoted:—100 kilos of finely ground pitchblende residue are heated with about 400 kilos of crude concentrated  $\text{H}_2\text{SO}_4$  for several hours, until the acid begins to fume. When the dark brown colour of the mixture has changed to light brown or grey, the mass is poured into 10-20 times its volume of  $\text{H}_2\text{O}$ , boiled, settled, and solution decanted. The residue is washed twice with water, collected on a filter, and dried. The residual mass (45-50 kilos) is now heated with 130-150 kilos of commercial NaOH in iron crucibles for 1-2 hours until thoroughly melted. The mass is boiled several times with  $\text{H}_2\text{O}$  (1,000 litres each time), decanted, and filtered.

The moist residue is boiled with 5 kilos of dilute (20 per cent.)  $\text{H}_2\text{SO}_4$ , filtered, and washed; 0.5 g. of crude sulphates remain.

The radium factory in Neulembach use this process with good success, recovering 97-98 per cent. of radium.

W. F. Bleecker and the Standard Chemical Co. of Pittsburg, U.S.A., suggest treating the **Carnotite** ore as follows (see U.S.A. Patents, 1,068,730, 1913, and 1,065,581, 1913):—The finely powdered carnotite ore is successively treated with (1) a solution of NaOH and  $\text{Na}_2\text{CO}_3$  to form partly soluble vanadates and insoluble sodium uranate. (2) The residue, after washing, is extracted with dilute HCl to produce radium, vanadyl, and uranyl chlorides. (3) Next  $\text{Na}_2\text{CO}_3$  is added, whereby  $\text{RaCO}_3$  is precipitated, sodium vanadate (partly soluble) and sodium uranyl carbonate (soluble) being simultaneously produced. (4) To the residue, after washing, HCl is added to produce  $\text{RaCl}_2$  (soluble) and vanadyl chlorides. (5) Lastly,  $\text{H}_2\text{SO}_4$  is added, the Ra being precipitated as  $\text{RaSO}_4$ , and the Va going into solution as soluble vanadyl sulphate. See under Vanadium, Chapter VIII.

F. Soddy, in his "Chemistry of the Radioelements," p. 45, recommends that the tedious and lengthy wet methods for extracting the barium-radium product from the mineral at present in use could with advantage be replaced in many cases

by simple reduction of the insoluble sulphates to sulphides in a current of coal gas, or other reducing atmosphere, followed by solution of the product in acid.

E. Ebler and W. Bender (*Zeits. anorg. Chem.*, 1913, **83**, 149-158) suggest reducing the dry powdered crude "sulphates" of radium, barium, etc., to sulphides by mixing with calcium hydride, pressing into a crucible, and kindling as in the aluminothermic method, when the following change takes place:— $\text{RaSO}_4 + 4\text{CaH}_2 = \text{RaS} + 4\text{CaO} + 4\text{H}_2$ . The reaction product is cooled, powdered, rapidly dissolved in hot dilute HCl, and the  $\text{H}_2\text{S}$  expelled by boiling. The Pb present remains undissolved as  $\text{PbS}$ , also  $\text{SiO}_2$  is insoluble. The whole of the radium is then separated as pure radium-barium chloride, by evaporating, if necessary, and treating with HCl gas until about 75 per cent. of the Ba is deposited. A total recovery of 75-80 per cent. of the Ra is claimed.

R. Sternlicht (*Chem. Zeit.*, 1914, **38**, 49), however, criticises adversely the method, on account of the technical difficulties evolved, the cost of the  $\text{CaH}_2$ , the rapid re-oxidation of the precipitated sulphides to sulphate, and the fact that it can only be applied to ores rich in radium and poor in barium.

**Separation of Radium and Barium.**—The last stage in the operations consists of the separation of the radium from the barium by fractional crystallisation of either the bromide or the chloride. Formerly this crystallisation was effected with the chloride, later the bromide was used instead, as the operations were much more rapid; but owing to the fact that the chloride is a much more stable compound than the bromide, and parts with its halogen much less readily on keeping, fractionation is now conducted on the chloride. To carry out this operation we proceed in the usual way, the operation depending on the fact that radium chloride is less soluble in hydrochloric acid than is barium chloride.

Kunheim & Co. (German Patent, 264, 901, 1912) propose to effect the separation of Ba and Ra by using such salts as picrates, bromates, and ferro-cyanides. As solvents, alcohol and acetic acid may be used instead of water.

E. Ebler and W. Bender (*Zeits. anorg. Chem.*, 1913, **84**, 77-91) suggest the use of hydrated manganese dioxide as an absorbent for radium-barium salts. The process, however, according to R. Sternlicht (*Chem. Zeit.*, 1914, **38**, 49), has not come into general use.

Most of the radium on the market is in the form either of chloride or of bromide. It is usually sealed up in tubes of thin glass, the reason for doing so being not only for safety, but also to prevent escape of the emanation, and with it its products, which together contribute themselves more than three times the activity of radium itself measured by  $\alpha$ -rays, and the whole of the activity measured by  $\beta$ - and  $\gamma$ -rays (see Table A above). It is essential that the salt, whether it be pure or whether it be mixed with barium salts, be quite dry before it is sealed up. If it is not, the increase in pressure inside the tube due to the formation of hydrogen and oxygen by the action of the radiations on the water may cause the tube to burst, and the material to be scattered about and lost.

Of the chemistry of radium compounds little need be said, except that they resemble very much the corresponding compounds of barium.

Radium sulphate is more insoluble than barium sulphate, radium chloride more insoluble in hydrochloric acid than barium chloride, radium bromide more insoluble in hydrobromic acid than barium bromide. Radium carbonate is easily soluble in hydrochloric acid. Radium metal has been prepared, but it is very rapidly oxidised, and is of strictly scientific interest only.

### The Separation of Ionium, Radiolead, and Polonium

Of these three bodies the most useful for medical purposes is **polonium**. Polonium is useful because it expels an  $\alpha$ -ray of moderately great penetrating power, and can be easily obtained pure and in a highly concentrated condition.

**Preparations of ionium** have also been placed on the market by a Hamburg firm, and it is very probable that for some technical purposes preparations of this body will be used in the future.

**Ionium** is the parent substance of radium. It is therefore found in all minerals which contain uranium and radium. Its chemistry may be stated accurately in a sentence. It is so similar in all properties to the element thorium that it is impossible for it to be separated from that body when once the two have

been mixed. In working up any mineral on a large scale, the ionium is quantitatively separated with the rare earth constituents, and in the fractionation of these bodies by the usual methods it associates itself quantitatively with thorium. The whole of the ionium constituent of any uranium mineral can therefore be obtained by fractionating the rare earth constituents of it, and separating out and purifying the thorium by the well-known methods. There is not the slightest risk that any of the ionium will associate itself with any body other than thorium.

Preparations of ionium have been obtained weighing several grammes, and equalling in  $\alpha$ -ray activity 30 milligrammes of radium chloride.

Most of these preparations, however, consist of thorium with a few per cent. of ionium only. Owing to a relatively great amount of an almost inactive body being associated with a small quantity of a very active body, much of the usefulness of the ionium is lost. Pure ionium can be obtained by working up a uranium mineral which contains no trace of thorium at all, but such minerals have not yet been located, though in many the amount of thorium present cannot be detected in the gramme or two of it used for making a quantitative analysis.

**Radiolead** is a name given to radium D, containing radium E and polonium in equilibrium with it, in other words, to an old preparation of radium D. The reason for its being called radiolead is that it was always found with the lead impurity of a uranium mineral. Radiolead is of technical importance only because it grows polonium. Neither radium D nor its product, radium E, expel any radiation except feebly penetrating  $\beta$ - and  $\gamma$ -rays, nor is it possible to obtain radium D free from the relatively large mass of lead which is separated with it from the mineral.

Radium D is so similar to lead in all its chemical and its physical properties that it is not possible for it to be separated from it, or even concentrated in a mixture of both substances. All uranium minerals, with one or two minor exceptions, contain lead as an impurity; the few which have no lead have none because the lead which it originally contained has been removed from it by percolating water or other natural agencies, which often remove at the same time a good proportion of the radium content, and of the radium D content. For this reason it is impossible to obtain pure radium D from a radium mineral. If a preparation of nearly pure radium D be wanted for any purpose it may be obtained as follows:—To an old solution of radium salt add a few milligrammes of lead in the form of nitrate free from sulphate, heat the solution to boiling, and add to it excess of a solution of  $\text{H}_2\text{S}$  in water. The whole of the radium D, radium E, and polonium which have formed in the radium solution are precipitated quantitatively with the lead as sulphide. This precipitate may be then filtered off and used as a source of radiation on the filter paper.

The only lead or other impurity associated now with the radiolead is the few milligrammes of lead that were added to the radium solution. If this operation be performed once only, a small quantity of the radium will be found present with the radiolead. This can be removed by dissolving the lead in acid, repeating the precipitation with  $\text{H}_2\text{S}$ , and filtering, the radium impurity remaining in the filtrate.

**The methods for the separation of polonium** from a mineral depend on the fact that polonium is the missing top member of the sulphur, selenium, and tellurium series (group VI. B of the Periodic Classification). The method for its separation from a preparation of radiolead depends on the great ease with which it is deposited on plates of metal when these are dipped into a solution containing it.

After tellurium, the body which polonium resembles most is bismuth. In any technical process of working up a uranium mineral it is necessary, therefore, to examine the **bismuth constituent** of the mineral when it is separated out, and from this to concentrate the polonium. Thus, from one ton of Joachimsthal pitchblende, about 3 kg. of bismuth oxychloride are obtained. This contains the greater part of the polonium content of the mineral. From it Mme. Curie separated the polonium from the bismuth by fractional precipitation of the basic



nitrate with water, by fractional precipitation from solutions made very acid with hydrochloric acid, and by sublimation *in vacuo*. Later, Marckwald separated it from bismuth and other impurities by immersing a plate of silver or of copper in a hydrochloric acid solution of all, the polonium being deposited on the plate in almost quantitative amount. He found also, by adding a small quantity of stannous chloride to the solution of polonium and impurities in hydrochloric acid, that the tellurium impurity, and with it the polonium, were precipitated. From this mixture most of the tellurium could be removed from the polonium by dissolving both in not too acid a solution, adding hydrazin hydrate (which precipitates the tellurium, but not the polonium), and precipitating the polonium from the solution by stannous chloride. This is at present the best method known for separating polonium from a mineral.

When polonium has to be separated from a preparation of radiolead, the procedure is much simpler. If the radiolead preparation contains much lead, all but a few milligrammes must be removed by fractional crystallisation of the nitrate from a solution of nitric acid. To carry this out the preparation of radiolead containing the lead is dissolved in nitric acid, and evaporated, till on cooling some of the lead crystallises out. Most of the polonium remains in the solution with the rest of the lead. This operation is then repeated several times, till only a small quantity of lead (a few milligrammes) remains. The solution can then be evaporated to dryness, and redissolved in the smallest quantity of hot water necessary to effect solution. In this solution is rotated a clean copper plate, varnished on one side with Brunswick black or other similar material to prevent deposition on it of the polonium. After about ten minutes the plate can be removed. The greater part of the polonium in the solution will be deposited on the plate. In many cases the proportion is as high as 95 per cent. If the amount of lead associated with the radiolead be small, the preliminary operation of removing the lead by fractional crystallisation may be omitted.

Preparations of polonium may be used for all purposes in which a very strong source of  $\alpha$ -rays in a concentrated form is required. Polonium possesses the advantage over ionium, that the former can be prepared in a more highly purified form than can the latter. Ionium, however, owing to its long half-value period, may be looked upon as being permanent in its activity. A preparation of polonium, on the other hand, decays, falling every 136 days to half value, only about one-seventh of the total amount at the beginning of a year existing at the end of it.

Other methods for purifying radium E and polonium are described by A. S. Russell and J. Chadwick (*Phil. Mag.*, 1914, 27, 112).

### The Separation of Mesothorium and Radiothorium from Thorium Minerals

The radioactive body, **mesothorium**, has come greatly to the fore within the last two or three years as a serious competitor with radium in the radium markets. Owing to the very large quantity of thorium used in the gas-mantle industry, in which, as has been stated above, mesothorium is a by-product, it will probably be very largely manufactured in the future. Owing to the fact, however, that thorium forms only a very small percentage of the constituents of monazite sand, and that its product, mesothorium, associates itself with the insoluble sulphate residues of the mineral, the extraction of mesothorium from monazite is a somewhat costly process. Another disadvantage which attaches to it is that it is not permanent, but decays, its half-value period being 5.5 years.

Mesothorium is identical in chemical properties with radium. Pure mesothorium behaves exactly as though it were radium. If mesothorium and radium are mixed together they cannot afterwards be separated.

To separate mesothorium, therefore, from any mineral, it is necessary only to add a little barium chloride to a solution of the mineral, to precipitate the

barium as sulphate from this solution, and to fractionate the insoluble sulphate precipitate by exactly the same methods as are used for fractionating radium.

If the mineral shows from its analysis that it contains barium, it is, of course, not necessary to add any barium salt to its solution.

All the methods employed at present in preparing mesothorium on a large scale are based on this general method.

For instance, in the first stage of the chemical treatment of monazite sand for the extraction of thorium the mineral is heated with about twice its own weight of sulphuric acid. The resultant mass, when cold, is treated with water and the whole left to settle. The thorium itself goes mainly into solution. Now if a little quantity of barium is added either before or during the treatment of the ore with sulphuric acid, the mesothorium will be separated from the soluble thorium after the treatment with water, associating itself with the difficultly soluble sulphates. Barium and mesothorium can then be separated from the other sulphates by the ordinary methods used for purifying barium under such conditions. The mesothorium is finally separated from barium by fractional crystallisation of the chloride. The preparations of mesothorium on the market are usually in the form of chloride sealed up in glass tubes. The impure preparations contain in addition both barium and radium. The purest contain radium only as impurity. The reason for the presence of the radium is, of course, that mesothorium and radium have the same chemical properties, and therefore all the radium of the mineral gets concentrated with the mesothorium. If the thorium mineral contained no uranium whatever there would be no radium content, but most thorium minerals (including monazite sand) contain a small percentage of uranium, and therefore some radium, and this is separated with the mesothorium. In most preparations of mesothorium now being sold about 80 per cent. of the activity of the whole preparation is due to the mesothorium, and as much as 20 per cent. to the radium with it. Weight for weight, however, the preparation contains about 99 per cent. radium chloride and 1 per cent. mesothorium chloride, the radium, having much the longer period of average life, being present in much greater mass than the mesothorium. The radiations from an old preparation of mesothorium are essentially the same in nature as those from radium. All three types of radiations are expelled by it. Mesothorium itself is rayless, but its first product, mesothorium 2, expels a powerful  $\beta$ - and  $\gamma$ -radiation. This body is very shortlived, forming radiothorium which, with its products, gives a powerful  $\alpha$ -radiation. This radiation can be made use of only when the preparation is removed from the tube, since the glass walls of the tube absorb most of the  $\beta$ -rays and all of the  $\alpha$ -rays emitted by the products.

Owing to the formation of the radiothorium, a body having a half-value period of about two years, and the fact that mesothorium itself has a half-value period of 5.5 years, the  $\alpha$ -ray activity of a preparation of mesothorium steadily increases for about 4 to 6 years. During this time the  $\beta$ - and  $\gamma$ -activity is augmented owing to the formation of thorium C and thorium D. After that time all three types of radiation decay in intensity, exponentially to zero, with a period of 5.5 years.

**Radiothorium**, the other important radioactive constituent of thorium minerals, cannot be separated directly from the mineral. The reason for this is that radiothorium and thorium have identical chemical properties. Nobody who has attempted the separation of these two bodies has been able, up to the present, to effect a separation or to detect the slightest difference in any of their chemical properties. The radiothorium of a mineral is, therefore, separated quantitatively with the thorium. The only method of preparing radiothorium is to prepare it from a quantity of mesothorium. A preparation of pure mesothorium, after being left for a year to grow radiothorium, is dissolved in a little hydrochloric acid. A solution of a small quantity of aluminium nitrate, or of any inorganic body which is precipitated by ammonia, is added to the solution, and the whole saturated with ammonia gas. The aluminium is precipitated as hydrate, and with it is precipitated

the whole of the radiothorium. The mesothorium, and any radium present, remain in solution. The amount of aluminium necessary to be added is simply enough to be conveniently filtered, *i.e.*, about a milligramme or two. Many of the preparations of commerce contain thorium, this body having been used instead of aluminium in the precipitation of radiothorium by ammonia.

Radiothorium has two uses in medical work: it is not only the producer of a constant supply of thorium emanation, but also the producer of the highly active deposit of thorium.

In order to get a plentiful supply of emanation from a preparation of radiothorium, the substance should be placed, in a slightly moist state, in a tube with narrow ends. By means of suitable apparatus a current of air may be passed over the preparation, removing much of its emanation, which may be inhaled or put to other use.

For many purposes in medical treatment with radioactive preparations a temporary activity only is required. For instance, it may be necessary for the patient to swallow some radioactive material. It would be manifestly unwise to put a valuable preparation to this use. This difficulty may be overcome by separating, by chemical means, thorium X from the radiothorium preparation. The whole of the thorium X may be easily removed by dissolving the radiothorium in acid and passing in ammonia gas. This precipitates the radiothorium and its nucleus quantitatively, leaving in solution the thorium X, which is chemically identical with radium and mesothorium. The ammonium salts may be removed by evaporation of the solution and ignition, and the thorium X may then be redissolved and used. The activity of the radiothorium is thus not destroyed, for in a month's time it has grown its equilibrium amount of thorium X again, and this quantity can be separated as before if it be necessary.

It may be pointed out that thorium X cannot be obtained in this way from mesothorium, owing to the identical properties of the two.

Radiothorium loses its activity much more quickly than mesothorium, falling to half value every two years. Thus after ten years only about 3 per cent. of the original quantity of material is left.

### Methods of Testing the Strength of Radioactive Bodies

The strength of any radioactive body is measured by the intensity either of its  $\alpha$ - or of its  $\gamma$ -rays, and all activities are referred to the  $\alpha$ -ray activity of 1 g. of radium in the form of metal, or to the  $\gamma$ -ray activity of the quantity of radium C in equilibrium with 1 g. of radium metal. The amount of radium emanation in equilibrium with 1 g. of pure radium metal is called a *curie*. Thus 5.8 millicuries of emanation is the amount of emanation in equilibrium with 5.8 mg. of radium metal, *i.e.*, with 7.6 mg. of radium chloride, or with 9.9 mg. of anhydrous radium bromide.

A curie expels per second the same number of  $\alpha$ -particles as 1 g. of radium metal. Since, however, radium A and C, both of which expel  $\alpha$ -particles, soon form in the emanation, a curie of emanation in equilibrium with its short-lived products expels per second three times as many  $\alpha$ -particles as does a gramme of radium freed from its products. The intensity of every product in the uranium-radium series should be expressed in terms of grammes or milligrammes of metallic radium. There can then be no doubt what is meant by the unit used. Formerly, activities were often expressed in terms of what were known as Mache units, and sometimes in terms of the  $\alpha$ -ray activity of uranium. Such units are not only unscientific, but also unbusinesslike, for they are not definite units which are accepted everywhere.

It is customary at the present time, for instance, to talk about 5 mg. of polonium. This does not mean 5 mg. of polonium by weight, but that quantity of polonium which is in equilibrium with 5 mg. of radium metal or 5 millicuries of emanation. Similarly 300 mg. of radium C means the quantity of radium C in equilibrium with 300 mg. radium metal or 300 millicuries of radium emanation.

Again, 4 mg. of ionium means the amount of ionium with which, in a mineral, 4 mg. of radium are in equilibrium. The amount by weight of any product of the uranium-radium series can always be obtained by multiplying its activity expressed in terms of milligrammes of radium metal by its period, and dividing by the period of radium, and *vice versa*.

Preparations of mesothorium and of radiothorium are standardised and sold in terms of the  $\gamma$ -ray activity of 1 mg. of radium C, *i.e.*, the  $\gamma$ -ray activity of the radium C in equilibrium with 1 mg. of radium metal. As the penetrating power of the  $\gamma$ -rays from the thorium preparations and from radium are not quite the same, it is usual to measure the intensity through 3 mm. of lead. Thus a preparation of radiothorium when in equilibrium with its product, thorium X, gives 50 divisions per minute in a  $\gamma$ -ray electroscope through a thickness of 3 mm. lead, when 1 mg. of radium chloride containing the emanation in equilibrium amount gives 12, then the strength of the radiothorium preparation is  $\frac{50 \times 226}{12 \times 297}$  mg. of radium at the date on which the measurements were made. Mesothorium preparations have their activities expressed in the same way.

This standardisation is now carried out for a small fee by experts at the **National Physical Laboratory, Teddington, in England.** Everybody buying radium, mesothorium, or radiothorium should insist on having the official certificates of its strength and purity furnished by this institution.

The strengths of preparations of ionium and of polonium, if very strong, may be measured by measuring the current a film of the material produces in the air of an ionisation box and comparing it with the current produced in the same ionisation box by a known quantity of a radium salt, the measurements of the current being determined by an electrometer. If the preparations are too weak to allow of this being done, the number of  $\alpha$ -particles expelled by a known area of the film may be compared with that expelled by a small quantity of radium, the measurements being made by the scintillation method.

The radium emanation content of a mineral, of any solid preparation, or of any solution containing it, is measured in a special emanation electroscope. The procedure consists essentially of getting the radium-containing solid completely into solution, expelling the radium emanation completely from it, allowing the emanation to accumulate in it for a definite time, say forty hours, transferring this quantity of emanation completely from the solution into an air-tight ionisation chamber, and measuring the activity of the emanation and its products three hours after it has been in this chamber by means of an electroscope. The electroscope is standardised by introducing a known quantity of emanation either from a small but known quantity of a radium salt, or from a uranium mineral, the ratio of the quantity of radium to that of uranium of which is known, allowing this emanation to remain in the chamber for three hours, and then measuring its activity. In this way the emanation content of any body can be expressed in terms of the amount of emanation in equilibrium with 1 mg. of radium element.

### Uses of Radioactive Substances in Medicine and in General

The chief use of radium and other radioactive bodies, apart from their use for strictly scientific investigation, is undoubtedly in medicine. A short account of their use in this department of science will therefore be given. Many medical men are much more optimistic in their opinion of the therapeutic value of these preparations than others, but there are certain facts of which there can be but little doubt.

Radium, especially when used in considerable quantity, has undoubtedly effected cures of surface cancers, warts, lupus, and ulcers. The reason for much of the former non-success in curing these diseases was the lack of a sufficient quantity of the active material. We are informed further that the emanation of radium when drunk or inhaled causes increased diuresis, and increased excretion of uric acid, and relieves patients suffering from gout, rheumatism, and diabetes.

It must be pointed out, however, that there are less expensive methods of curing these diseases than the employment of radioactive substances. The object that medical men have in view in experimenting with radium is to cure **cancer**. To further this object a radium institute has been founded in London, and similar institutes are being formed in the provinces, at which medical men may obtain radioactive preparations with which to experiment.

The results obtained by treating cancer with radium have been astonishingly successful. In all cases the condition of the patient is relieved. In the worst cases radioactive preparations, when applied to the diseased part, have acted as local anæsthetics in removing the pain. In several cases every sign of the cancer has been completely removed. Experiments have been in progress for a short time only, and therefore a considerable time must be allowed to elapse before even the most successfully treated case is described as a cure. Already (September 1914) there are three hospitals in the kingdom in which non-medical men, trained in radioactive chemistry, are working in conjunction with medical men on this great problem.

It is the possibility that radium will be a permanent cure for cancer that has stimulated the search for radium minerals over the earth, and has caused neither money nor pains to be spared to bring to the doctor's hand as much of the valuable material as possible. Until quantities of the order of 10 g. can be used in medicine the possibilities of radium as a curer of cancer and malignant diseases of a like nature cannot be known. It is as reasonable to expect some of the small quantities of radium to cure the disease to which they have been applied as that ten cubic centimeters of cold water should quench the thirst of a thirsty man.

For internal use the preparations used are generally either radium emanation or thorium B, C, and D. In both these the physiological effects produced are due to the  $\alpha$ -rays from these bodies.

The radium emanation may either be inhaled directly from an atmosphere laden with emanation, or taken in the form of gas dissolved in mineral water.

There is at present on the market a small chamber in which a patient may sit, the air of which is kept permanently supplied with emanation diffusing from a strong force of radium placed on the floor. The radioactive water is made either by dissolving a known quantity of radium carbonate or chloride completely, and diluting down by the ordinary methods till each litre of solution contains about  $10^{-6}$  g. of radium (or stronger if necessary), and with it, of course, after it has been bottled up for a month, the emanation in equilibrium amount or "Radium water" can be made to contain emanation only by simply pumping off the emanation from a known quantity of radium and dissolving it in a large quantity of water by shaking. In the latter case much larger doses may be taken for the same cost.

If a patient is required to take internally only the active deposit of radium, *i.e.*, radium B and C, it may be collected on a pill, or on anything that is easily swallowed, by exposing the pill for some hours to a large quantity of the emanation, the emanation is then removed and may be used again for the same purpose.

This is not so easily accomplished with the emanation of thorium, and, therefore, it is best to separate the active deposit of thorium, *i.e.*, thorium B, C, and D, chemically from radiothorium as described above. It is then taken in the liquid form dissolved in some solvent.

For external purposes, the substance used depends upon the particular disease which is being attacked. If a strong source of  $\alpha$ -rays are required, preparations of ionium, or of polonium, in thin films on plates of metal, make excellent sources. If  $\alpha$ -rays are required with  $\gamma$ -rays, the source which must be used is a thin tube of glass, or of quartz, containing radium emanation, the tube being so thin that the  $\alpha$ -rays are able to escape from it ( $\alpha$ -ray tubes).

Whenever  $\alpha$ -rays are used, the preparation must be placed so near the part that is being treated that the rays are able to exert their full effect. Sometimes radium, or radiothorium, is immersed in the pores of a blanket or other similar material, so that the emanation diffuses out of the dry fabric without any of the parent substance being lost.

If  $\gamma$ -rays only are required, sealed tubes of radium salts, of radium emanation, of mesothorium, or of radiothorium can be used. Of these sources radiothorium is the least concentrated, and radium emanation the most concentrated. The latter, however, decays almost to zero in a month. A source of mesothorium, if free from barium, is much more concentrated than a source of pure radium. Radium, radium emanation, and mesothorium are the sources of  $\gamma$ -rays used in work on cancer.

It must be emphasised that all radium, or radioactive preparations containing quantities as small as  $10^{-9}$  of a gramme of radium, can be of little therapeutic value. Ointments, pills, radioactive blankets, etc., containing quantities of material of this order, are of no more value than the same preparations lacking the radioactive constituent.

Preparations of radium, mixed with zinc sulphide, emit a greenish-yellow light, due to the bombardment of the zinc sulphide crystals by the  $\alpha$ -particles from the radium and its products.

This mixture has been used for giving a permanent illumination to keyholes, to the hands of a watch or clock, etc., so that these articles may be seen easily in the dark.

### The Prices of Materials

The present (1913) price of radium is about £24 per milligramme of radium element. All radium preparations are priced on this basis, though actually no radium is sold in the metallic form. Reckoned on this basis a milligramme of radium chloride should cost about £18. 10s., and a milligramme of anhydrous bromide, £14. There was formerly little diminution of charge because a radium preparation is impure. Thus 325 mg. of radium-barium chloride containing 24 per cent. of radium chloride costs £ $\frac{24}{100} \times 325 \times 18\frac{1}{2}$ , *i.e.*, simply the price of the pure radium chloride it contains. When the preparation contained a few per cent. only of radium a larger diminution was made in the price. At the present time the difference in price between equal quantities of pure and

impure radium is considerable. The price of radium bromide in 1902 was 5s. a milligramme, this rose next year to 6s., and later to 20s., which was the price in 1904. Since that time the price has steadily risen to what it is to-day. The question whether the price of radium will advance further is not only an interesting one, it is a very practical one.

Rutherford, whose knowledge of radioactivity is unrivalled, says in his book, published in 1913, that "the present price of radium is very high, and bears no relation to the cost of separation of the radium from uranium minerals. The present price is artificial. There seems to be no reason why the present abnormally high prices of radium should be ultimately maintained."

On the other hand, C. A. Parsons, whose knowledge of the resources of the United States is very great, declares that at the present time "it is impossible to predict whether the price will go up or down, or remain stationary." The great increase in production of radium that is bound to happen in the next years in the United States would tend, other things being equal, to lower the price. Again, the competition of mesothorium, which is being put on the market in increasing quantities every year, should also tend to lower the price. Mesothorium, however, for reasons difficult to understand, is less popular with medical men than radium. But the uses and demands for radium are apparently developing at an even greater rate than the supply. Also, as has been pointed out above, the present supply of the mineral is limited.

The one thing that would lower the price seems to the writer to be the adaptation of X-rays (resembling  $\gamma$ -rays), cathode rays (resembling  $\beta$ -rays), and canal rays (resembling  $\alpha$ -rays) to effect exactly the same physiological effects and the same curative powers which are produced by radioactive materials. This at present seems unlikely, but it is a question for the future.

The only radium mineral selling in large quantities at present is the 2 per cent.  $U_3O_8$  carnotite ore from Colorado. This sells at Hamburg for about £19 per ton (1913). The equilibrium amount of radium element in this material is at least 4 mg. per ton, which, when extracted, can be sold for about £100. Since the price of the raw material from which this quantity of radium is extracted is about £19, there is a margin of £80 for the cost of extraction, the profit of the extractor and of the agents through whose hands the material must pass before it reaches the buyer. The present prices of the other radium ores are not of much importance, owing to the present drift of the radium-extracting industry from Austria and France to the United States.

The present (1913) price of mesothorium is about £5 per milligramme, where, by milligramme, is not meant milligramme of mesothorium, but the quantity of mesothorium, the  $\gamma$ -ray activity of which through 3 mm. of lead is equal to that from 1 mg. of radium chloride through the same thickness.

The price of preparations of radiothorium vary according to the purity of the material, but it is of the order of £2 or £3 per milligramme equivalent in  $\gamma$ -rays of radium chloride.

The price of the monazite sand has not been influenced by the fact that these radioactive bodies are extracted from it.

**Output of Radium Compounds.**—It is difficult to estimate the quantity of radium compounds produced annually, but the following details may be of service in this connection. According to S. Fischer (*Min. Ind.*, 1913, 22, 657) the Austrian production of radium salts, during 1912, amounted to about 5 gm. as compared with 2.65 gm. produced in 1911. The total European production, in 1913, was about 4 gm., whilst the Australian ores yielded 2 gm. It has been estimated that the quantity of uranium ores exported from the United States, in 1913, was sufficient to produce 8.97 gm. of radium chloride.

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A PRACTICAL TREATISE

BY

GEOFFREY MARTIN, Ph.D., D.Sc., F.C.S.

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PRODUCTS," ETC.

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